

# A Resource Theory for Work and Heat

Carlo Sparaciari,<sup>1,\*</sup> Jonathan Oppenheim,<sup>1,†</sup> and Tobias Fritz<sup>2,‡</sup>

<sup>1</sup>*Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom*

<sup>2</sup>*Max Planck Institute for Mathematics in the Sciences, Leipzig, Germany,  
and Perimeter Institute for Theoretical Physics, Waterloo, Canada*

(Dated: October 13, 2016)

Several recent results in the field of quantum thermodynamics have been obtained using the tools of quantum information theory and resource theories. So far, the resource theories utilised to describe quantum thermodynamics have assumed the existence of an infinite thermal reservoir, by declaring that thermal states at some background temperature come for free. Here, we propose a resource theory of quantum thermodynamics without a background temperature, so that no states at all come for free. We apply this resource theory to the case of many non-interacting systems, and show that states are classified by their entropy and average energy. This implies that thermodynamics can be described in a two-dimensional convex set that we call the *energy-entropy diagram*. The answers to many resource-theoretic questions about thermodynamics can be read off from this diagram, such as the efficiency of a heat engine consisting of finite reservoirs or the rate of conversion between two states. This allows us to consider a resource theory which puts work and heat on an equal footing, and serves as a model for more general resource theories.

## I. INTRODUCTION

To make precise statements about thermodynamics, particular at the quantum scale, we need to precisely define what thermodynamics is. In particular, we have to specify what an experimenter is allowed to do to take a system from one state into another. This specification defines a resource theory, something which has been used explicitly to successfully describe thermodynamic phenomena occurring at the microscopic scale [1–15], although any line of research which specifies what the rules of thermodynamics are, can be said to define a resource theory [16–25]. These theories typically consist of a state space and a set of allowed operations that can be performed on the states (see e.g. [26–30] for reviews).

The resource theories developed so far for quantum thermodynamics are based on assuming that thermal states (Gibbs states) at a fixed background temperature come for free. In these theories, states are classified by their free energy, and this quantity also equals the amount of work that can be extracted from many copies of a given state [2, 5, 19, 21]. However, the existence of an infinite thermal reservoir cannot always be taken for granted [31, 32]. In some applications, such as many types of engines, the system under consideration operates on such short timescales that it must be considered a closed system. In other applications, the environment is finite and its state changes due to the interaction with the system, for example when a power plant dumps large amounts of heat to the environment. It seems therefore imperative to develop thermodynamics as a resource theory *without* assuming the existence of an infinite thermal reservoir. This is the aim of the present paper.

The set of allowed operations in our resource theory is potentially much broader than the one an experimentalist can implement, as any energy-preserving unitary is allowed. Therefore, our theory primarily delineates fundamental limitations to what is possible in “real life”. Moreover, the results we present are concerned with the asymptotic regime, i.e. the limit of many non-interacting identical system. This follows the abstract approach to resource theories developed in [33]. We believe the results here derived to be achievable using a more implementable set of operations, as in the resource theory of Thermal Operations [14], when only changing the energy levels of the system, and thermal contact with a heat bath is allowed. However, for the time being, our results should be seen as upper limits, only achievable in idealised conditions.

In addition to providing a general framework for thermodynamics in the absence of an infinite bath, we prove that quantum states are asymptotically equivalent under energy-preserving unitaries if and only if they have same entropy and average energy, see Thm. 1. Due to this equivalence, we interpret the specification of entropy and average energy of a state as the description of a thermodynamic *macrostate*. Thermodynamics in the asymptotic limit is then studied by only considering the set of macrostates, which we call the *energy-entropy diagram*. This diagram is a complete description of thermodynamics in the asymptotic limit. For example, we use it to study rates of conversion between two states of a closed system, and to propose a definition of the work and heat exchanged while interconverting two states using a finite thermal reservoir and a battery. The resulting expressions for work and heat, Eqs. (8), recover the standard ones in the limit of an infinite thermal reservoir, when its temperature only changes infinitesimally.

\* carlo.sparaciari.14@ucl.ac.uk

† j.oppenheim@ucl.ac.uk

‡ fritz@mis.mpg.de

## II. FRAMEWORK AND ALLOWED OPERATIONS

The systems we consider in our resource theory consist of  $n$  copies of a single  $d$ -level system described by  $C^d$  (a *qudit*) with fixed Hamiltonian  $H$ ; both  $d$  and  $H$  are parameters of the theory. We assume the total Hamiltonian  $H_{\text{tot}}$  of the global system to be the sum of single-qudit Hamiltonians  $H$ , each of them acting on a different copy, thereby making the different copies of the system non-interacting. The resource objects of our theory are quantum states on such an  $n$ -qudit system, over all  $n \in \mathbb{N}$ . The allowed operations for turning one such state into another are all the global unitaries  $U$  acting on the total system which are energy-preserving in the sense that  $[U, H_{\text{tot}}] = 0$ . This takes into account the first law of thermodynamics, but otherwise assumes perfect control over the system. Hence all conversions of states are reversible by definition. For simplicity, we assume the Hamiltonian to be fixed throughout, without any possibility of changing it. In Thm. 1 we also permit the use of an ancilla system of sublinear size and energy spectrum which can be initialized in an arbitrary state and gets discarded at the end. When talking about rates of conversion, we permit discarding subsystems that are decoupled from the rest.

This resource theory describes the thermodynamics of closed systems in the absence of an infinite thermal reservoir, in contrast to the theory of Thermal Operations [1–5, 19]. In fact, Thermal Operations allow us to add an arbitrary number of thermal states  $\tau_\beta = Z_\beta^{-1} e^{-\beta H}$  at a given temperature  $\beta^{-1}$ , with  $Z_\beta = \text{Tr}[e^{-\beta H}]$  the partition function of the system. By not allowing this possibility, we obtain a theory which can describe, among other things, systems in contact with a finite reservoir in which thermal states are themselves a valuable resource.

## III. ASYMPTOTIC EQUIVALENCE AND THE ENERGY-ENTROPY DIAGRAM

Our resource theory clearly has many conserved quantities: since the allowed operations are unitaries, if a state is converted into another then they must live on the same number of qudits, and have the same spectrum. Moreover, since our unitaries are energy-preserving, the states must have the same *distribution* over the energy levels, or equivalently the same moments of energy. This makes our theory very restrictive.

However, at the asymptotic level the situation is quite different, and we have that two states can be interconverted if and only if they have same entropy and average energy<sup>1</sup>. In particular, we say that a state  $\rho$  is *asymptot-*

*ically equivalent* to another state  $\sigma$ , and write  $\rho \asymp \sigma$ , if one of the conditions of the following theorem holds.

**Theorem 1.** *For states  $\rho$  and  $\sigma$  on any quantum system of dimension  $d$  with given Hamiltonian  $H$ , the following are equivalent:*

- (a) *The states have equal entropy and average energy,  $S(\rho) = S(\sigma)$  and  $E(\rho) = E(\sigma)$ ,*
- (b) *There exists an ancilla system  $A$  of size  $O(\sqrt{n} \log n)$  whose Hamiltonian  $H_A$  satisfies  $\|H_A\| \leq O(n^{2/3})$  with state  $\eta$  as well as an energy-preserving unitary  $U$  such that*

$$\|\text{Tr}_A [U(\rho^{\otimes n} \otimes \eta)U^\dagger] - \sigma^{\otimes n}\|_1 \xrightarrow{n \rightarrow \infty} 0. \quad (1)$$

where  $\|X\|_1 = \text{Tr}[\sqrt{X^\dagger X}]$  is the trace norm,  $E(\rho) = \text{Tr}[H\rho]$  is the average energy, and  $S(\rho) = -\text{Tr}[\rho \log \rho]$  is the von Neumann entropy.

It is essential that the number of qudits composing the ancilla, as well as the bound on the spectrum of  $H_A$ , is sublinear in the number of copies of the system  $n$ . In fact, the constraints on the size and energy of the ancilla are related, respectively, to the amount of entropy and energy we can exchange with the system. Since both these quantities are sublinear in  $n$ , one can show that the ancilla contribution per single copy of the system tends to 0 as  $n \rightarrow \infty$ . This sketches the reason why asymptotic equivalence implies equal entropy and average energy.

To show the opposite direction, we need to implement a protocol turning  $\rho^{\otimes n}$  into something close (in trace norm) to  $\sigma^{\otimes n}$ . This is achieved by applying a energy-preserving unitary operation over the  $n$  copies of the system and the additional ancillary system  $A$ . This ancilla is composed by three subsystems, each of them in charge of a different aspect of the transformation. The first subsystem provides a source of randomness, used to modify the spectrum of the state; its state is maximally mixed, and its Hamiltonian is trivial. The second subsystem is used as a register, and allows us to dilate slightly irreversible operations on the global system to reversible ones. Its initial state is pure, and the Hamiltonian is trivial. The third subsystem makes the transformation energy-preserving, and allows for introducing/removing coherence in the energy eigenbasis. It has a non-trivial Hamiltonian, and its state is in a uniform superposition of the energy eigenstates. Overall, the ancilla satisfies the properties listed in (b). The formal proof is given in the Supplemental Material.

Thus we can interconvert asymptotically, using the set of allowed operations, between states with same entropy  $S$  and average energy  $E$ . Consequently, we can classify any quantum state asymptotically in terms of these two quantities only. Such a passage from quantum to macroscopic states is at the core of thermodynamics in the guise of the passage from *microstates* to *macrostates*. Our result seems to capture this, despite being built on

<sup>1</sup> Notice that these quantities are precisely the *asymptotically continuous* ones [34].

the idealised assumption of non-interacting copies. From now on, we identify the many-copy limit that one takes when considering asymptotic equivalence with the standard macroscopic limit of thermodynamics.

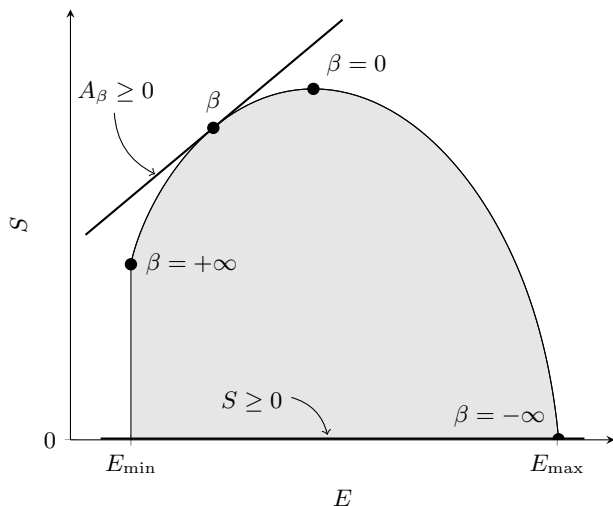


FIG. 1. The energy-entropy diagram representing the state space of a quantum system with Hamiltonian  $H$ , degenerate in the ground state (vertical line). The physical points are inside the grey area. Each point  $(E, S)$  represents an equivalence class of microstates, i.e. a single macrostate. Ineq. (2a), postulating the nonnegativity of entropy, is satisfied by the points above the  $E$ -axis. For a given  $\beta$ , the Ineq. (2b) is satisfied by those points below the drawn line which is tangent to the physical region, and goes through the point  $(E(\tau_\beta), S(\tau_\beta))$  with slope  $\beta$ .

When macroscopic thermodynamics is considered, it is therefore sufficient to focus on the pair of numbers  $(E, S)^2$ , and we can avoid to use the description in terms of the quantum state  $\rho$ . The set of all these pairs forms a two-dimensional convex set that we call the *energy-entropy diagram*. Fig. 1 illustrates an example diagram<sup>3</sup> for a particular choice of  $d$  and  $H$ . The extreme points of these diagrams are given by the macrostates associated to the thermal states  $\tau_\beta$ , for any  $\beta \in \mathbb{R} \cup \{\pm\infty\}$ , and to any pure ground state and pure maximally excited state of  $H$ . Alternatively, we can describe the diagram by the family of linear inequalities that bound it; in this formulation, it turns out that a pair of values  $(E, S)$  belongs to the

energy-entropy diagram if and only if

$$S \geq 0, \quad (2a)$$

$$A_\beta \geq 0 \quad \forall \beta \in \mathbb{R}, \quad (2b)$$

where we refer to  $A_\beta := \beta E - S + \log Z_\beta$  as the  $\beta$ -*athermality*. This quantity is linked to the free energy  $F_\beta = E - \beta^{-1}S$  by the relation  $A_\beta = \beta(F_\beta - F_\beta(\tau_\beta))$ , and it can also be expressed as the difference in free entropy (see Ref. [36]) between the macrostate  $(E, S)$  and the macrostate of  $\tau_\beta$ .

Macroscopic thermodynamics as a resource theory can now be analysed with the energy-entropy diagram and its characterisation in terms of inequalities. To give a concrete example, we illustrate the computation of the rate of conversion between the single-qudit states  $\rho$  and  $\sigma$ . Given  $n$  copies of  $\rho$ , we want to evaluate the maximum number of copies  $m$  of  $\sigma$  that we can obtain while using energy-preserving unitaries and discarding subsystems. The conversion can be achieved by using the asymptotic equivalence between the states  $\rho^{\otimes n}$  and  $\sigma^{\otimes m} \otimes \phi$ , where  $\phi$  is a garbage state from which we cannot extract any additional  $\sigma$  state, and  $n, m \gg 1$ . We define the maximal rate of conversion from  $\rho$  to  $\sigma$  as

$$R_{\max}(\rho \rightarrow \sigma) = \sup \left\{ \frac{m}{n} \mid \rho^{\otimes n} \succ \sigma^{\otimes m} \otimes \phi \right\}, \quad (3)$$

where the optimisation is performed over all possible garbage states  $\phi$ . By representing the optimisation problem in the energy-entropy diagram, and by making use of the Ineqs. (2), one can show that

**Theorem 2.** *The maximal rate from  $\rho$  to  $\sigma$  is equal to the minimal ratio of the value of an additive monotone on  $\rho$  versus its value on  $\sigma$ ,*

$$R_{\max}(\rho \rightarrow \sigma) = \min \left\{ \frac{S(\rho)}{S(\sigma)}, \inf_{\beta \in (-\infty, +\infty)} \frac{A_\beta(\rho)}{A_\beta(\sigma)} \right\}, \quad (4)$$

where the minimization is only over those fractions for which the denominator is nonzero.

This expression is an instance of a general rate formula for resource theories [33, Thm. 8.24]. When the maximal rate is  $\frac{S(\rho)}{S(\sigma)}$ , the garbage state is given by a pure state  $|E\rangle^{\otimes(n-m)}$ . When the maximal rate is equal to  $\frac{A_\beta(\rho)}{A_\beta(\sigma)}$ , the garbage state is  $\phi = \tau_\beta^{\otimes(n-m)}$ .

#### IV. WORK AND HEAT FOR FINITE SIZE RESERVOIRS

We now consider the problem of converting  $n \gg 1$  copies of a state  $\rho$  into the same number of copies  $n$  of a state  $\sigma$ , as opposed to previous case (Thm. 2) in which the number of copies of the final state was different from  $n$ . The transformation is performed using a finite size

<sup>2</sup> The energy-entropy diagram can be extended in order to incorporate the number of qudits on which a given state lives. This generalisation, which forms a convex cone in  $\mathbb{R}^3$ , is considered in Lemma 15 of the Supplemental Material.

<sup>3</sup> It is intriguing that as a convex set, the energy-entropy diagram closely resembles colour space (i.e. the chromaticity diagram) [35, Sec. 35-4]. We are currently not aware of any deeper explanation of this coincidence.

thermal reservoir and a battery as extra systems for storing “heat”, in the form of entropy changes, and “work”, in the form of energy changes. In the following we assume that, while mapping  $\rho$  into  $\sigma$ , work is extracted. This is not always the case, and to consider the opposite situation it is sufficient to swap the initial and final state of the battery.

Consider a tripartite closed system, consisting of the main system, the thermal reservoir, and the battery, each of them provided with the same single-system Hamiltonian  $H^4$ . We take the initial state of this total system to be

$$\omega_{\text{in}} = \rho^{\otimes n} \otimes \tau_{\beta_1}^{\otimes m} \otimes |E_{\text{min}}\rangle\langle E_{\text{min}}|^{\otimes \ell}, \quad (5)$$

where the reservoir is composed of a suitable number  $m$  of thermal states at some temperature  $\beta_1^{-1}$ , and the battery is composed of a suitable number  $\ell$  copies of the ground state of the Hamiltonian; both numbers will be determined later. Similarly, the final state of the total system is

$$\omega_{\text{fin}} = \sigma^{\otimes n} \otimes \tau_{\beta_2}^{\otimes m} \otimes |E_{\text{max}}\rangle\langle E_{\text{max}}|^{\otimes \ell}, \quad (6)$$

where the temperature of the reservoir is now some other temperature  $\beta_2^{-1}$ , and some energy has been stored in the battery, which is in the maximally excited state of  $H$ .

We think of  $\beta_1$  and  $\beta_2$  as fixed, while the sizes of the thermal reservoir  $m$  and of the battery  $\ell$  will depend on  $\rho$  and  $\sigma$ . These can be adjusted such that  $\omega_{\text{in}}$  and  $\omega_{\text{fin}}$  have the same entropy and average energy, which makes them asymptotically equivalent; concretely, we have

$$\frac{m}{n} = \frac{S(\sigma) - S(\rho)}{S(\tau_{\beta_1}) - S(\tau_{\beta_2})}, \quad (7)$$

and a similar expression for  $\frac{\ell}{n}$  (see the Supplemental Material for more detail). Since taking the asymptotic limit is equivalent to considering the case  $m, n, \ell \gg 1$ , this means that  $\omega_{\text{in}}$  and  $\omega_{\text{fin}}$  are  $\varepsilon$ -close if and only if  $m$  and  $\ell$  are determined in this way. Despite the assumption  $m \gg 1$ , our reservoir is finite in the sense that the number of thermal states needed per copy of the system,  $\frac{m}{n}$ , is constant and does not diverge for large  $n$ .

These conditions let us define notions of work and heat in a standard way for the conversion of  $\rho$  into  $\sigma$ . Namely, the work extracted is given by the energy difference between the final and initial state of the battery, that is, in the current case,  $W_{\beta_1, \beta_2}(\rho \rightarrow \sigma) = \frac{\ell}{n}(E_{\text{max}} - E_{\text{min}})$ , where we divide by  $n$  in order to normalise per copy of  $\rho$  and  $\sigma$ . The heat we provide is equal to the energy difference between the initial and final state of the reservoir,  $Q_{\beta_1, \beta_2}(\rho \rightarrow \sigma) = \frac{m}{n}(E(\tau_{\beta_1}) - E(\tau_{\beta_2}))$ .

Using the previously obtained expressions for  $\frac{m}{n}$  and  $\frac{\ell}{n}$  results in

$$W_{\beta_1, \beta_2}(\rho \rightarrow \sigma) = \beta_{\text{eff}}^{-1}(A_{\beta_{\text{eff}}}(\rho) - A_{\beta_{\text{eff}}}(\sigma)), \quad (8a)$$

$$Q_{\beta_1, \beta_2}(\rho \rightarrow \sigma) = \beta_{\text{eff}}^{-1}(S(\sigma) - S(\rho)), \quad (8b)$$

where these definitions apply to any two states  $\rho$  and  $\sigma$ . We define an effective temperature  $\beta_{\text{eff}}^{-1}$  depending on the initial and final temperatures of the reservoir,

$$\beta_{\text{eff}} := \frac{S(\tau_{\beta_1}) - S(\tau_{\beta_2})}{E(\tau_{\beta_1}) - E(\tau_{\beta_2})}. \quad (9)$$

This equation can be interpreted as the slope of the line connecting the points on the boundary of the energy-entropy diagram corresponding to the thermal states  $\tau_{\beta_1}$  and  $\tau_{\beta_2}$ .

Therefore the work that we can extract is the free energy difference between the initial and final state of the system at the effective temperature  $\beta_{\text{eff}}^{-1}$ . Moreover, due to this definition of work and heat, the first law of thermodynamics holds automatically in the form

$$E(\rho) - E(\sigma) = Q_{\beta_1, \beta_2}(\rho \rightarrow \sigma) - W_{\beta_1, \beta_2}(\rho \rightarrow \sigma). \quad (10)$$

If we consider the limit of an infinite reservoir, so that the temperature changes only infinitesimally, we find that the amount of work and heat exchanged is equal to the standard one. In fact, if we assume  $\beta_2 = \beta_1 + \varepsilon$ , for  $|\varepsilon| \ll 1$ , then the effective inverse temperature is  $\beta_{\text{eff}} = \beta_1 + O(\varepsilon)$ , and Eqs. (8) specialise to the standard expressions for work and heat when we are given an infinite thermal reservoir at fixed temperature  $\beta_1^{-1}$ .

## V. CONCLUSION

Our resource theory for thermodynamics does not make use of an infinite thermal reservoir. Therefore, it is suitable for analysing state transformations both when the system is decoupled from the environment, Eq. (3), and when the system is interacting with a finite reservoir, Eqs. (8). Moreover, the theory provides a rigorous mathematical explanation (through the Thm. 1) to the fact that, when dealing with macroscopic thermodynamics, we can describe the state of a system with few observables (for instance, energy and entropy). Our model generalises the one presented in Ref. [5], where asymptotic state transformations are considered when an infinite reservoir is present.

The results we obtain are valid in a specific regime delineated by several idealised assumptions, such as the complete freedom in the choice of the energy-preserving unitaries, the presence of many non-interacting and identical copies of the system, and the constraint of a fixed Hamiltonian for each system. One can think of dropping some of these assumptions, and for example investigate the theory when arbitrary states and interactions are allowed (often called the single-shot regime), or when one

<sup>4</sup> This setup turns out to be quite general. For instance, in the Supplemental Material we use it in order to bound the efficiency of heat engines and refrigerators operating between two finite size reservoirs, Sec. B 5.

has a much more realistic class of operations not requiring such fine grained control of system and bath [14].

The asymptotic equivalence result presented in Eq. (1) is obtained with the help of a sublinear ancillary system. One might think that with this ancilla we could *embezzle* work [4, 37, 38], that is, we could extract work from the ancillary system in such a way as to leave its state essentially unchanged. However, we solve the embezzling problem by also constraining the energy spectrum of the ancilla to be sublinear in the number of copies of the main system.

Recently, resource theories with multiple conserved quantities (even non-commuting ones), have been investigated within the framework of quantum thermodynamics [15, 36, 39]. However, in these models, emphasis is put on different notions of work, each of them related to a different conserved quantity. Our theory, on the other

hand, considers only energy<sup>5</sup>. We expect that our approach can be extended more or less straightforwardly so as to cover multiple commuting conserved quantities as well; generalising our theory to a treatment of multiple non-commuting conserved quantities may present new challenges.

## VI. ACKNOWLEDGEMENT

We would like to thank Lidia del Rio, Joe Renes, Matteo Smerlak and Rob Spekkens for helpful discussions. CS is supported by the EPSRC Centre for Doctoral Training in Delivering Quantum Technologies. Research at Perimeter Institute is supported by the Government of Canada through Industry Canada and by the Province of Ontario through the Ministry of Economic Development and Innovation.

- 
- [1] D. Janzing, P. Wocjan, R. Zeier, R. Geiss, and T. Beth, “Thermodynamic cost of reliability and low temperatures: Tightening Landauer’s principle and the second law,” *Int. J. Theor. Phys.*, vol. 39, pp. 2717–2753, Dec. 2000.
  - [2] M. Horodecki and J. Oppenheim, “Fundamental limitations for quantum and nanoscale thermodynamics,” *Nature Communications*, vol. 4, 2013.
  - [3] M. Horodecki, P. Horodecki, and J. Oppenheim, “Reversible transformations from pure to mixed states and the unique measure of information,” *Phys. Rev. A*, vol. 67, no. 6, p. 062104, 2003.
  - [4] F. G. S. L. Brandao, M. Horodecki, N. H. Y. Ng, J. Oppenheim, and S. Wehner, “The second laws of quantum thermodynamics,” *Proc. Natl. Acad. Sci.*, vol. 112, no. 11, pp. 3275–3279, 2015.
  - [5] F. G. S. L. Brandao, M. Horodecki, J. Oppenheim, J. M. Renes, and R. W. Spekkens, “Resource theory of quantum states out of thermal equilibrium,” *Physical Review Letters*, vol. 111, no. 25, 2013.
  - [6] N. Yunger Halpern and J. M. Renes, “Beyond heat baths: Generalized resource theories for small-scale thermodynamics,” *Phys. Rev. E*, vol. 93, p. 022126, Feb. 2016.
  - [7] M. P. Woods, N. Ng, and S. Wehner, “The maximum efficiency of nano heat engines depends on more than temperature,” 2015. arXiv:1412.3828 [quant-ph].
  - [8] P. Cwiklinski, M. Studzinski, M. Horodecki, and J. Oppenheim, “Limitations on the Evolution of Quantum Coherences: Towards Fully Quantum Second Laws of Thermodynamics,” *Phys. Rev. Lett.*, vol. 115, p. 210403, Nov. 2015.
  - [9] M. Lostaglio, K. Korzekwa, D. Jennings, and T. Rudolph, “Quantum Coherence, Time-Translation Symmetry, and Thermodynamics,” *Phys. Rev. X*, vol. 5, p. 021001, Apr. 2015.
  - [10] H. Wilming, R. Gallego, and J. Eisert, “Second law of thermodynamics under control restrictions,” *Phys. Rev. E*, vol. 93, p. 042126, Apr. 2016.
  - [11] G. Gour, M. P. Muller, V. Narasimhachar, R. W. Spekkens, and N. Yunger Halpern, “The resource theory of informational nonequilibrium in thermodynamics,” *Physics Reports*, 2015.
  - [12] L. Masanes and J. Oppenheim, “A derivation (and quantification) of the third law of thermodynamics,” 2014. arXiv:1412.3828 [quant-ph].
  - [13] A. M. Alhambra, L. Masanes, J. Oppenheim, and C. Perry, “The second law of quantum thermodynamics as an equality,” 2016. arXiv:1601.05799 [cond-mat, quant-ph].
  - [14] C. Perry, P. Cwiklinski, J. Anders, M. Horodecki, and J. Oppenheim, “A sufficient set of experimentally implementable thermal operations,” 2015. arXiv:1511.06553 [cond-mat, quant-ph].
  - [15] N. Y. Halpern, P. Faist, J. Oppenheim, and A. Winter, “Microcanonical and resource-theoretic derivations of the Non-Abelian Thermal State,” *arXiv:1512.01189 [cond-mat, physics:quant-ph]*, 2015.
  - [16] G. E. Crooks, “Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences,” *Phys. Rev. E*, vol. 60, pp. 2721–2726, Sept. 1999.
  - [17] O. C. O. Dahlsten, R. Renner, E. Rieper, and V. Vedral, “Inadequacy of von Neumann entropy for characterizing extractable work,” *New J. Phys.*, vol. 13, no. 5, p. 053015, 2011.
  - [18] L. d. Rio, J. Aberg, R. Renner, O. Dahlsten, and V. Vedral, “The thermodynamic meaning of negative entropy,” *Nature*, vol. 474, no. 7349, pp. 61–63, 2011.
  - [19] J. Aberg, “Truly work-like work extraction via single-shot analysis,” *Nature Communications*, vol. 4, p. 1925, 2013.

---

<sup>5</sup> Or any other *single* conserved quantity—if one replaces e.g. “energy” by “angular momentum” throughout our work, our results are still equally correct and meaningful.

- [20] P. Faist, F. Dupuis, J. Oppenheim, and R. Renner, “The minimal work cost of information processing,” *Nature Communications*, vol. 6, p. 7669, July 2015.
- [21] P. Skrzypczyk, A. J. Short, and S. Popescu, “Work extraction and thermodynamics for individual quantum systems,” *Nature Communications*, vol. 5, 2014.
- [22] K. Korzekwa, M. Lostaglio, J. Oppenheim, and D. Jennings, “The extraction of work from quantum coherence,” *New J. Phys.*, vol. 18, no. 2, p. 023045, 2016.
- [23] V. Narasimhachar and G. Gour, “Low-temperature thermodynamics with quantum coherence,” *Nat Commun*, vol. 6, p. 7689, July 2015.
- [24] R. Gallego, J. Eisert, and H. Wilming, “Thermodynamic work from operational principles,” 2015. arXiv:1504.05056 [cond-mat, physics:math-ph, physics:quant-ph].
- [25] L. J. Schulman and U. V. Vazirani, “Molecular Scale Heat Engines and Scalable Quantum Computation,” in *Proceedings of the Thirty-first Annual ACM Symposium on Theory of Computing*, STOC ’99, pp. 322–329, ACM, 1999.
- [26] M. Horodecki and J. Oppenheim, “(Quantumness in the context of) resource theories,” *Int. J. Mod. Phys. B*, vol. 27, p. 1345019, 2012.
- [27] B. Coecke, T. Fritz, and R. W. Spekkens, “A mathematical theory of resources,” 2014. arXiv:1409.5531 [quant-ph].
- [28] L. del Rio, L. Krämer, and R. Renner, “Resource theories of knowledge,” 2015. arXiv:1511.08818 [quant-ph].
- [29] S. Vinjanampathy and J. Anders, “Quantum Thermodynamics,” 2015. arXiv:1508.06099 [quant-ph].
- [30] J. Goold, M. Huber, A. Riera, L. del Rio, and P. Skrzypczyk, “The role of quantum information in thermodynamics—a topical review,” *J. Phys. A*, vol. 49, p. 143001, 2016.
- [31] H. Tajima and M. Hayashi, “Optimal efficiency of heat engines with finite-size heat baths,” 2014. arXiv:1405.6457 [quant-ph].
- [32] J. Richens, A. M. Alhambra, and L. Masanes in preparation, 2016.
- [33] T. Fritz, “Resource convertibility and ordered commutative monoids,” *Mathematical Structures in Computer Science*, to appear. arXiv:1504.03661 [math.OC].
- [34] B. Synak-Radtke and M. Horodecki, “On asymptotic continuity of functions of quantum states,” *Journal of Physics A: Mathematical and General*, vol. 39, no. 26, p. L423, 2006.
- [35] R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, vol. 1. Addison-Wesley, 1963.
- [36] Y. Guryanova, S. Popescu, A. J. Short, R. Silva, and P. Skrzypczyk, “Thermodynamics of quantum systems with multiple conserved quantities,” 2015. arXiv:1512.01190 [quant-ph].
- [37] W. van Dam and P. Hayden, “Universal entanglement transformations without communication,” *Physical Review A*, vol. 67, no. 6, 2003.
- [38] N. H. Y. Ng, L. Mančinska, C. Cirstoiu, J. Eisert, and S. Wehner, “Limits to catalysis in quantum thermodynamics,” *New Journal of Physics*, vol. 17, no. 8, p. 085004, 2015.
- [39] M. Lostaglio, D. Jennings, and T. Rudolph, “Thermodynamic resource theories, non-commutativity and maximum entropy principles,” 2015. arXiv:1511.04420 [quant-ph].
- [40] C. Shannon, “A mathematical theory of communication,” *Bell System Technical Journal*, vol. 27, no. 3, pp. 379–423, 1948.
- [41] B. Schumacher, “Quantum coding,” *Phys. Rev. A*, vol. 51, no. 4, pp. 2738–2747, 1995.
- [42] M. A. Nielsen and I. L. Chuang, *Quantum Computation and Quantum Information*. Cambridge University Press, 2010.
- [43] I. Devetak, A. W. Harrow, and A. Winter, “A resource framework for quantum Shannon theory,” *IEEE Trans. Inf. Theory*, vol. 54, no. 10, pp. 4587–4618, 2008.
- [44] E. Breuillard, B. Green, and T. Tao, “Small doubling in groups,” in *Erdős Centennial*, vol. 25 of *Bolyai Society Mathematical Studies*, pp. 129–151, Springer, 2013.
- [45] N. F. Ramsey, “Thermodynamics and statistical mechanics at negative absolute temperatures,” *Phys. Rev.*, vol. 103, pp. 20–28, 1956.
- [46] G. M. Ziegler, *Lectures on polytopes*, vol. 152 of *Graduate Texts in Mathematics*. Springer, 1995.
- [47] S. Goldstein, J. L. Lebowitz, C. Mastrodonato, R. Tumulka, and N. Zanghi, “Normal typicality and von Neumann’s quantum ergodic theorem,” *Proc. Royal Soc. A*, vol. 466, no. 2123, pp. 3203–3224, 2010.
- [48] J. Barrett, “Information processing in general probabilistic theories,” *Phys. Rev. A*, vol. 75, p. 032304, 2007.
- [49] H. Barnum, J. Barrett, M. Krümm, and M. P. Müller, “Entropy, majorization and thermodynamics in general probabilistic theories,” *Electronic Proceedings in Theoretical Computer Science*, vol. 195, 2015.
- [50] G. Chiribella and C. M. Scandolo, “Entanglement and thermodynamics in general probabilistic theories,” *New J. Phys.*, vol. 17, no. 10, p. 103027, 2015.
- [51] A. E. Allahverdyan, R. Balian, and T. M. Nieuwenhuizen, “Maximal work extraction from finite quantum systems,” *Europhysics Letters (EPL)*, vol. 67, no. 4, pp. 565–571, 2004.
- [52] E. T. Jaynes, “Information theory and statistical mechanics,” *Physical review*, vol. 106, no. 4, p. 620, 1957.
- [53] R. Alicki and M. Fannes, “Entanglement boost for extractable work from ensembles of quantum batteries,” *Physical Review E*, vol. 87, no. 4, 2013.

## SUPPLEMENTAL MATERIAL

The Supplemental Material is divided in two main sections. Sec. A is devoted to the proof of our main technical result, namely, the asymptotic equivalence of quantum states under energy-preserving unitary operations (presented in the main text as Theorem 1). This result is first proved for systems with trivial (completely degenerate) Hamiltonian, see Theorem 4, and it is later proved in the general case of arbitrary Hamiltonian, see Theorem 6. In Sec. B we reconstruct macroscopic thermodynamics starting from the asymptotic equivalence of quantum states. Specifically, in Sec. 1 we show that, due to Theorem 6, any quantum system can be described, in the limit of many copies, merely in terms of the macroscopic observables energy and entropy. In Sec. B2 we extend this macroscopic description by introducing a further parameter, which plays the role of an amount of substance. The addition of this parameter allows the theory to describe situations in which the number of systems changes during a transformation. In Sec. B3 we show how a thermodynamic state can always be described by a convex combination of other states, thus recasting macroscopic thermodynamics as a general probabilistic theory, although the mixing described by these convex combinations does not correspond to stochastic mixtures, but rather to forming composite systems. Sec. B4 is devoted to the definition of work and heat when a finite-size thermal reservoir is present. We also show that the amount of work and heat exchanged during a transformation tends to the classical one when the size of the thermal reservoir becomes infinite. In Sec. B5 we use the results about work and heat to characterise the ultimate efficiency that heat engines and refrigerators can achieve when operating with finite-size reservoirs. Finally, in Sec B6 we study the optimal rate of conversion between many copies of two quantum states (Theorem 2 in main text), when no additional resources (such as work or heat) are provided, and we can only discard part of the system.

### Appendix A: Asymptotic equivalence of states under energy-preserving unitaries

#### 1. Overview

We show in this section that two states of a quantum system are asymptotically equivalent under energy-preserving unitaries if and only if they have the same entropy and average energy. We say that two states are asymptotic equivalent when we can approximately map many identical copies of one state into the same number of copies of the other state, by applying a global unitary operation which preserves the energy. The precise statement is in Theorem 6.

The main difficulty in proving Theorem 6 consists in showing that when two states have same energy and entropy, then they can be asymptotically mapped one into the other. To prove this implication, we devise a protocol which maps (many copies of) one state into the other, provided that they have the same energy and entropy. We now summarise the protocol, in order to provide a simple and physical idea of its mechanism to the reader. We divide the protocol in two parts, one concerning the case of trivial Hamiltonian, the other concerning the case of non-trivial Hamiltonian.

When the system has a trivial Hamiltonian, we can act on it by means of any unitary operation, and the only assumption we need to make on the two states  $\rho$  and  $\sigma$  is that they have same entropy. Since we work in the asymptotic regime, where we take the tensor product of many copies of these states, we can use the tools developed in Shannon theory [40–42]. In particular, due to the central limit theorem, we can replace the many-copy states  $\rho^{\otimes n}$  and  $\sigma^{\otimes n}$  with their typical states, Eqs. (A6) and (A7). The use of the typical states highly simplifies the protocol, since in this way we can divide the Hilbert space into a small number of subspaces with common properties. State conversion is achieved in the protocol by mapping the probability distribution of the initial typical state into the one of the final typical state. This is done by introducing an ancillary system with trivial Hamiltonian, whose size is  $O(\sqrt{n \log n})$ , in the maximally mixed state. This ancilla provides a source of randomness, and we modify the probability distribution of the initial state by applying a global unitary operation on system and ancilla, and tracing out the ancilla. However, a unitary operation can be used only if the transformation is reversible. To assure that this is the case, another ancillary system is introduced, acting as a register. Again, the size of this second ancillary system is  $O(\sqrt{n \log n})$ , and the Hamiltonian is trivial. The details of the protocol are in the proof of Theorem 4.

When the system has a non-trivial Hamiltonian, we have to reduce the set of allowed unitary operations to the sole energy-preserving ones (the ones that commute with the Hamiltonian). With these operations, we can devise a protocol which approximately converts many copies of  $\rho$  into  $\sigma$  when the two states have same entropy and energy. The protocol which performs this asymptotic transformation is analogous to the one for trivial Hamiltonian. The difference is that in this case we have to add an additional ancillary system with non-trivial Hamiltonian, with which we can exchange both energy and coherence. This ancilla allows us to approximately implement any unitary on the system by applying an energy-preserving unitary on both system and ancilla. Due to the constraints on the energy and entropy of the initial and final state, and to the central limit theorem, we achieve that the size of this additional ancilla is  $O(\sqrt{n \log n})$ . Moreover, the spectrum of the ancillary Hamiltonian is bounded by  $O(n^{\frac{2}{3}})$ , so that we can

only modify the amount of energy by a sublinear amount. The details of the protocol are in the proofs of Lemma 5 and Theorem 6. To conclude, it is worth noting that none of the three ancillary systems depends in any way on the state  $\rho$  or  $\sigma$ , meaning that the transformation can be performed with the same ancillae for any initial and final state.

## 2. Asymptotic equivalence of quantum states

Before getting to thermodynamics, it helps to consider an easier case first: two states of a quantum system are many-copies equivalent under unitaries if and only if they have the same entropy. This is what we show first in Theorem 4. We begin with a simple lemma on randomness extraction which we will apply afterwards to approximate the typical set of one distribution by a coarse-graining of the typical set of another. We use the min-entropy, the Hartley entropy, and the Rényi entropy at parameter  $-\infty$ ,

$$H_\infty(p) = -\log \max_x p_x, \quad H_0(p) = \log |\{x \mid p_x > 0\}|, \quad H_{-\infty}(p) = -\log \min_x p_x.$$

**Lemma 3.** *Let  $(X, p)$  and  $(Y, q)$  be finite probability spaces. Then there exists a map  $f : X \rightarrow Y$  such that*

$$\|f_*(p) - q\|_1 \leq 2^{H_0(q) - H_\infty(p)}, \quad (\text{A1})$$

and

$$|f^{-1}(y)| \leq 2^{H_{-\infty}(p)} \left( 2^{-H_\infty(q)} + 2^{-H_\infty(p)} \right) \quad (\text{A2})$$

for all  $y \in Y$ .

Here,  $f_*(p)$  is the distribution on  $Y$  that one obtains by coarse-graining  $p$  via application of  $f$ , that is, by gathering in different sets the elements of  $X$ , obtaining a new distribution over a smaller space  $Y$ . The  $\|\cdot\|_1$  is the total variation distance, i.e. the classical version of the trace distance.

*Proof.* We choose an arbitrary enumeration of the elements of  $X$  as  $x_1, \dots, x_n$ , and construct  $f$  in piecemeal by defining  $f(x_1), \dots, f(x_n)$  one at a time. At the  $i$ -th step, we define  $f(x_i)$  to be equal to an arbitrary  $y \in Y$  whose probability has not yet been completely covered by the  $p_x$  that lie in the preimage  $f^{-1}(y)$  of the partially defined  $f$ , in the sense that

$$q_y > \sum_{x \in f^{-1}(y)} p_x,$$

where the sum is only over those  $x \in X$  for which  $f(x)$  has already been defined and is equal to  $y$ . Finding such a  $y$  is always possible since the normalisation of  $p$  equals the normalisation of  $q$ . The crucial property of the  $f$  thus constructed is that the total probability in a fibre  $f^{-1}(y)$  is never significantly larger than  $q_y$ ,

$$\sum_{x \in f^{-1}(y)} p_x \leq q_y + \max_x p_x. \quad (\text{A3})$$

This implies  $|f^{-1}(y)| \cdot \min_x p_x \leq q_y + \max_x p_x$ , resulting in (A2). To bound the total variation distance, we also use (A3),

$$\|f_*(p) - q\|_1 = \sum_y \max \left\{ 0, \sum_{x \in f^{-1}(y)} p_x - q_y \right\} \leq \sum_y \max_x p_x = |Y| \cdot \max_x p_x.$$

Since we can assume  $q$  to have full support without loss of generality, this is the desired inequality (A1).  $\square$

Turning to quantum information, we use the term “size” of a system to talk about the logarithm of its Hilbert space dimension, i.e. the number of qubits needed to realise it, and write  $S(\rho) = -\text{Tr}[\rho \log \rho]$  for the von Neumann entropy of a state  $\rho$ .

**Theorem 4** (Asymptotic classification of states). *For states  $\rho$  and  $\sigma$  on any quantum system of dimension  $d$ , the following are equivalent:*

- (a) *The states have equal entropy,  $S(\rho) = S(\sigma)$ .*



(b) There exists an ancilla system of size  $O(\sqrt{n \log n})$  with state  $\eta$  as well as a unitary  $U$  such that

$$\|\text{Tr}_{\text{anc}}[U(\rho^{\otimes n} \otimes \eta)U^\dagger] - \sigma^{\otimes n}\|_1 \xrightarrow{n \rightarrow \infty} 0. \quad (\text{A4})$$

(c) There exists an ancilla system of size  $o(n)$ , with states  $\eta$  and  $\nu$  as well as unitaries  $U$  and  $V$  such that

$$\|\text{Tr}_{\text{anc}}[U(\rho^{\otimes n} \otimes \eta)U^\dagger - V(\sigma^{\otimes n} \otimes \nu)V^\dagger]\|_1 \xrightarrow{n \rightarrow \infty} 0. \quad (\text{A5})$$

That is, up to things that happen on an ancilla of sublinear size, two states on a system are many-copies equivalent if and only if they have the same entropy. Condition (b) is a set of requirements on such a many-copies equivalence that we believe to be roughly minimal; in particular, the number of qubits needed to implement the ancilla system grows only barely faster than  $O(\sqrt{n})$ , and in fact the particular growth rate of  $O(\sqrt{n \log n})$  is an arbitrary choice and can be replaced by any function that grows faster than  $\sqrt{n}$ . Condition (c), in contrast, is a more permissive notion of many-copy equivalence that is still strong enough to imply (a), but it does not provide a different physical intuition than (b).

The  $\text{Tr}_{\text{anc}}[U(\cdot \otimes \eta)U^\dagger]$  form channels which are close to unitary in the sense of being implementable with only a sublinear ancilla; these are precisely the channels of subexponential Kraus rank. It may be interesting to study such channels in their own right, and there may be relations to [43].

*Proof.* The implication from (b) to (c) is trivial.

Assuming (c), the claim  $S(\rho) = S(\sigma)$  can be proven as follows. Let  $D$  be the dimension of the ancilla system. Then using the fact that adding or discarding the ancilla cannot change the entropy by more than  $\log(D)$ ,<sup>6</sup> we obtain, writing  $\varepsilon$  for the left-hand side of (A5),

$$\begin{aligned} |S(\rho) - S(\sigma)| &= \frac{1}{n} |S(\rho^{\otimes n}) - S(\sigma^{\otimes n})| \leq \frac{1}{n} |S(\rho^{\otimes n} \otimes \eta) - S(\sigma^{\otimes n} \otimes \nu)| + 2 \frac{\log(D)}{n} \\ &= \frac{1}{n} |S(U^\dagger(\rho^{\otimes n} \otimes \eta)U) - S(V^\dagger(\sigma^{\otimes n} \otimes \nu)V)| + 2 \frac{\log(D)}{n} \\ &\leq \frac{1}{n} |S(\text{Tr}_{\text{anc}}[U^\dagger(\rho^{\otimes n} \otimes \eta)U]) - S(\text{Tr}_{\text{anc}}[V^\dagger(\sigma^{\otimes n} \otimes \nu)V])| + 4 \frac{\log(D)}{n} \\ &\stackrel{(\text{A10})}{\leq} \frac{1}{n} (\log(d^n)\varepsilon + O(1)) + 4 \frac{\log(D)}{n} = O(\varepsilon) + O(n^{-1}) + 4 \frac{\log(D)}{n}. \end{aligned}$$

where the last estimate is by Fannes' inequality. Since  $\varepsilon \rightarrow 0$  as  $n \rightarrow \infty$  while  $D$  grows only subexponentially, it follows that  $|S(\rho) - S(\sigma)|$  is smaller than any positive number, and therefore  $S(\rho) = S(\sigma)$ .

To show that (a) implies (b), we can assume by unitary invariance that  $\rho$  and  $\sigma$  are diagonal in the same basis, where they are given by  $\rho = \text{diag}(p_1, \dots, p_d)$  and  $\sigma = \text{diag}(q_1, \dots, q_d)$ . In other words, we are in a classical situation involving finite probability spaces with distributions  $p = (p_1, \dots, p_d)$  and  $q = (q_1, \dots, q_d)$ , and we therefore use classical notation and terminology for the remainder of the proof, and write  $n_i$  for the number of times that outcome  $i$  occurs upon sampling from  $p^{\otimes n}$  or  $q^{\otimes n}$ . The central limit theorem guarantees that for  $p^{\otimes n}$ , the set of outcomes that are strongly typical in the sense that

$$n_i \in \left[ \left( n - \sqrt{n \log n} \right) p_i, \left( n + \sqrt{n \log n} \right) p_i \right] \quad (\text{A6})$$

has a total probability that approaches 1 as  $n \rightarrow \infty$ . Let  $T_p$  denote this typical set of outcomes and  $p_{\text{typ}}$  the resulting normalised distribution on typical outcomes that one obtains by conditioning on typicality. Similarly, let  $T_q$  be the strongly typical set for  $q^{\otimes n}$ , corresponding to outcome frequencies  $n_i$  restricted by

$$n_i \in \left[ \left( n - \sqrt{n \log n} \right) q_i, \left( n + \sqrt{n \log n} \right) q_i \right], \quad (\text{A7})$$

and  $q_{\text{typ}}$  the associated typical distribution. By bounding the lowest and the highest probability of any outcome in this strongly typical set, it is straightforward to show the following chain of inequalities,

$$nS(p) \left( 1 - \sqrt{\frac{\log n}{n}} \right) \leq H_\infty(p_{\text{typ}}) \leq H_0(p_{\text{typ}}) \leq H_{-\infty}(p_{\text{typ}}) \leq nS(p) \left( 1 + \sqrt{\frac{\log n}{n}} \right), \quad (\text{A8})$$

<sup>6</sup> More precisely, by the fact that the conditional entropy of the ancilla given the system is at most  $\log(D)$  in absolute value.

where we still write  $S(p) = H_1(p)$  for the Shannon entropy. The analogous bounds hold for  $q_{\text{typ}}$ . Note that the individual probabilities of the typical outcomes may still vary by a factor of up to  $2^{2\sqrt{n \log n} S(p)}$ , so that the typical distributions  $p_{\text{typ}}$  and  $q_{\text{typ}}$  may still be far from uniform. The strong typicality inequalities (A6) and (A7) themselves will not be used again; all that we need are the Rényi entropy bounds (A8) and that the probability of typicality approaches 1 as  $n \rightarrow \infty$ .

Now let  $r_1$  be the uniform distribution on  $3\sqrt{n \log n} S(p)$  many ancilla bits, rounded to the closest integer; in the following, we ignore the irrelevant rounding error. This results in the bounds

$$nS(p) + 2\sqrt{n \log n} S(p) \leq H_\infty(p_{\text{typ}} \otimes r_1) \leq H_{-\infty}(p_{\text{typ}} \otimes r_1) \leq nS(p) + 4\sqrt{n \log n} S(p)$$

Hence by Lemma 3, we can find  $f : T_p \times \{0, 1\}^{3\sqrt{n \log n} S(p)} \rightarrow T_q$  such that

$$\|f_*(p_{\text{typ}} \otimes r_1) - q_{\text{typ}}\|_1 \leq 2^{H_0(q_{\text{typ}}) - H_\infty(p_{\text{typ}} \otimes r_1)} \leq 2^{-\sqrt{n \log n} S(p)}$$

by (A1), which decays superpolynomially in  $n$ . Thanks to (A2),  $f$  can be implemented using a register ancilla of dimension at most

$$2^{H_{-\infty}(p_{\text{typ}} \otimes r_1)} \left( 2^{-H_\infty(q_{\text{typ}})} + 2^{-H_\infty(p_{\text{typ}} \otimes r_1)} \right) \leq 2^{5\sqrt{n \log n} S(p)} + 2^{2\sqrt{n \log n} S(p)} = 2^{O(\sqrt{n \log n})},$$

which is initially taken to carry an arbitrary deterministic distribution  $r_2$  and gets utilised to dilate  $f$  to a bijection.

We now put  $r := r_1 \otimes r_2$ , so that our total ancilla still has size  $O(\sqrt{n \log n})$ . We take  $U$  to be given by the action of  $f$  on the system and first ancilla, dilated to a bijection by the second ancilla. Since  $f_*$  is contractive, we have

$$\|f_*(p \otimes r_1) - q\|_1 \leq \|p_{\text{typ}} - p\|_1 + \|q_{\text{typ}} - q\|_1 + \|f_*(p_{\text{typ}} \otimes r_1) - q_{\text{typ}}\|_1 \xrightarrow{n \rightarrow \infty} 0,$$

since each individual term tends to 0. This establishes (A4) in classical notation.  $\square$

Getting to thermodynamics, we now also want to take energy preservation into account. To this end, we develop a method to turn every unitary into an energy-preserving unitary, while achieving approximately the same conversion of resource states. This relies on a protocol modelled after [5, Appendix E]. For finite sets of numbers  $\mathcal{A}, \mathcal{B} \subseteq \mathbb{R}$ , we consider the sumset  $\mathcal{A} + \mathcal{B} := \{a + b \mid a \in \mathcal{A}, b \in \mathcal{B}\}$ , as studied in additive combinatorics [44], and similarly also the difference set  $\mathcal{A} - \mathcal{B} = \{a - b \mid a \in \mathcal{A}, b \in \mathcal{B}\}$ . Furthermore, we write  $\|\mathcal{A}\| := \max_{a \in \mathcal{A}} |a|$ . And from now on, we also use  $\rho \approx_\varepsilon \sigma$  as a shorthand for  $\|\rho - \sigma\|_1 \leq \varepsilon$ .

**Lemma 5** (Achieving energy preservation). *Let  $0 < \delta < 1$  and suppose that  $\mathcal{L}, \mathcal{M} \subseteq \mathbb{R}$  are finite sets of numbers such that*

$$|\mathcal{M} + \mathcal{L}| \leq (1 + \delta)|\mathcal{M}|, \quad |\mathcal{M} - \mathcal{L}| \leq (1 + \delta)|\mathcal{M}|. \quad (\text{A9})$$

*Given a quantum system with Hamiltonian  $H$ , suppose that  $\rho$  and  $\sigma$  are states supported on energy levels in  $\mathcal{L}$ , and that there is a unitary  $U$  such that  $U\rho U^\dagger \approx_\delta \sigma$ . Then there is an ancilla system of size  $O(\log |\mathcal{M}|)$  with  $\|H_{\text{anc}}\| \leq 4\|\mathcal{M}\|$  and state  $\eta$  as well as an energy-preserving unitary  $\tilde{U}$  on the joint system, that is*

$$[\tilde{U}, H + H_{\text{anc}}] = 0,$$

*such that*

$$\text{Tr}_{\text{anc}}[\tilde{U}(\rho \otimes \eta)\tilde{U}^\dagger] \approx_{4\delta} \sigma.$$

Interestingly, what makes this difficult to prove are the quantum coherences that  $\rho$  and  $\sigma$  may have between the energy levels: in the classical case in which neither  $\rho$  nor  $\sigma$  has any coherence across energy levels, a unitary can easily be made energy-preserving by adding an ancilla in an initial state which can absorb any energy difference that may arise.

*Proof.* We do this by distinguishing two cases: first, the case that  $\sigma$  has no coherences across energy levels; second, the case that  $\rho$  has no such coherences. In each case, we will use an ancilla of size  $O(\log |\mathcal{M}|)$  with  $\|H_{\text{anc}}\| \leq 2\|\mathcal{M}\|$  and obtain a trace distance bound of  $2\delta$ . This is sufficient, since in the general case we can choose an arbitrary state  $\tau$  without energy coherences which has the same spectrum (with multiplicities) as that of  $\rho$  or  $\sigma$ , and compose the protocols constructed in the two cases, first from  $\rho$  to  $\tau$  and then from  $\tau$  to  $\sigma$ . This results in the claimed bounds.

Let the spectral decomposition of the system's Hamiltonian be  $H = \sum_{\lambda \in \text{sp}(H)} \lambda P_\lambda$ , with  $P_\lambda$  the projection onto the corresponding energy eigenspace.

Case 1:  $\sigma$  has no coherences across energy levels, i.e.  $P_\lambda \sigma P_\mu = 0$  if  $\lambda \neq \mu$ .

In this case, let the ancilla space be  $\mathcal{H}_{\text{anc}} := \mathbb{C}^{|\mathcal{M}-\mathcal{L}|}$  with Hamiltonian given by  $H_{\text{anc}} = \sum_{h \in \mathcal{M}-\mathcal{L}} h|h\rangle\langle h|$ . By (A9) and  $\delta < 1$ , the ancilla size is indeed  $\log |\mathcal{M}-\mathcal{L}| = O(\log |\mathcal{M}|)$  and moreover  $\|H_{\text{anc}}\| \leq 2|\mathcal{M}|$ . We take the initial ancilla state to be pure  $\eta := |\psi\rangle\langle\psi|$ , and given by the Hadamard state

$$|\psi\rangle := |\mathcal{M}-\mathcal{L}|^{-1/2} \sum_{h \in \mathcal{M}-\mathcal{L}} |h\rangle.$$

Furthermore, let  $\tilde{U}$  be any energy-preserving dilation of the energy-preserving partial isometry

$$\tilde{V} := \sum_{h \in \mathcal{M}} \sum_{\lambda, \mu \in \mathcal{L}} P_\lambda U P_\mu \otimes |h-\lambda\rangle\langle h-\mu|,$$

so that  $\tilde{U}$  decomposes into a direct sum of  $\tilde{V}$  plus an arbitrary other partial isometry. Then  $\tilde{V}(\rho \otimes \eta)\tilde{V}^\dagger$  evaluates to

$$\begin{aligned} & |\mathcal{M}-\mathcal{L}|^{-1} \sum_{h_1, h_2 \in \mathcal{M}} \sum_{\lambda_1, \lambda_2, \mu_1, \mu_2 \in \mathcal{L}} (P_{\lambda_1} U P_{\mu_1} \otimes |h_1-\lambda_1\rangle\langle h_1-\mu_1|) \\ & \quad \times \left( \rho \otimes \sum_{\ell_1, \ell_2 \in \mathcal{M}-\mathcal{L}} |\ell_1\rangle\langle\ell_2| \right) (P_{\mu_2} U^\dagger P_{\lambda_2} \otimes |h_2-\mu_2\rangle\langle h_2-\lambda_2|) \\ &= |\mathcal{M}-\mathcal{L}|^{-1} \sum_{\lambda_1, \lambda_2, \mu_1, \mu_2 \in \mathcal{L}} P_{\lambda_1} U P_{\mu_1} \rho P_{\mu_2} U^\dagger P_{\lambda_2} \otimes \sum_{h_1, h_2 \in \mathcal{M}} |h_1-\lambda_1\rangle\langle h_2-\lambda_2| \\ &\approx_\delta |\mathcal{M}-\mathcal{L}|^{-1} \sum_{\lambda_1, \lambda_2 \in \mathcal{L}} P_{\lambda_1} \sigma P_{\lambda_2} \otimes \sum_{h_1, h_2 \in \mathcal{M}} |h_1-\lambda_1\rangle\langle h_2-\lambda_2| \\ &= |\mathcal{M}-\mathcal{L}|^{-1} \sum_{\lambda \in \mathcal{L}} P_\lambda \sigma P_\lambda \otimes \sum_{h \in \mathcal{M}} |h-\lambda\rangle\langle h-\lambda|, \end{aligned}$$

where the last step uses the assumption of absence of coherence in  $\sigma$ . The resulting reduced state is therefore

$$\text{Tr}_{\text{anc}} [\tilde{V}(\rho \otimes \eta)\tilde{V}^\dagger] \approx_\delta \sum_{\lambda \in \mathcal{L}} \frac{|\mathcal{M}|}{|\mathcal{M}-\mathcal{L}|} P_\lambda \sigma P_\lambda = \frac{|\mathcal{M}|}{|\mathcal{M}-\mathcal{L}|} \sigma \geq (1-\delta)\sigma.$$

In particular, the total weight of  $\rho \otimes \eta$  on the orthogonal complement of the support of  $\tilde{V}$  is at most  $\delta$ . This shows that

$$\left\| \text{Tr}_{\text{anc}} [\tilde{U}(\rho \otimes \eta)\tilde{U}] - \sigma \right\|_1 \leq 2\delta.$$

Case 2:  $\rho$  has no coherences across energy levels, i.e.  $P_\lambda \rho P_\mu = 0$  if  $\lambda \neq \mu$ . It turns out that we can proceed very similarly.

In this case, let the ancilla space be  $\mathcal{H}_{\text{anc}} := \mathbb{C}^{|\mathcal{M}+\mathcal{L}|}$  with Hamiltonian given by  $H_{\text{anc}} = \sum_{h \in \mathcal{M}+\mathcal{L}} h|h\rangle\langle h|$ . By (A9) and  $\delta < 1$ , the ancilla size is indeed  $\log |\mathcal{M}+\mathcal{L}| = O(\log |\mathcal{M}|)$  and moreover  $\|H_{\text{anc}}\| \leq 2|\mathcal{M}|$ . We take the initial ancilla state to be pure  $\eta := |\psi\rangle\langle\psi|$ , and given by the Hadamard state

$$|\psi\rangle := |\mathcal{M}+\mathcal{L}|^{-1/2} \sum_{h \in \mathcal{M}+\mathcal{L}} |h\rangle.$$

Furthermore, let  $\tilde{U}$  to be any energy-preserving dilation of the energy-preserving partial isometry

$$\tilde{V} := \sum_{h \in \mathcal{M}} \sum_{\lambda, \mu \in \mathcal{L}} P_\lambda U P_\mu \otimes |h+\mu\rangle\langle h+\lambda|,$$

so that  $\tilde{U}$  decomposes into a direct sum of  $\tilde{V}$  plus an arbitrary other partial isometry. Then  $\tilde{V}(\rho \otimes \eta)\tilde{V}^\dagger$  evaluates

to

$$\begin{aligned}
& |\mathcal{M} + \mathcal{L}|^{-1} \sum_{h_1, h_2 \in \mathcal{M}} \sum_{\lambda_1, \lambda_2, \mu_1, \mu_2 \in \mathcal{L}} (P_{\lambda_1} U P_{\mu_1} \otimes |h_1 + \mu_1\rangle\langle h_1 + \lambda_1|) \\
& \quad \times \left( \rho \otimes \sum_{\ell_1, \ell_2 \in \mathcal{M} + \mathcal{L}} |\ell_1\rangle\langle \ell_2| \right) (P_{\mu_2} U^\dagger P_{\lambda_2} \otimes |h_2 + \lambda_2\rangle\langle h_2 + \mu_2|) \\
&= |\mathcal{M} + \mathcal{L}|^{-1} \sum_{\lambda_1, \lambda_2, \mu_1, \mu_2 \in \mathcal{L}} P_{\lambda_1} U P_{\mu_1} \rho P_{\mu_2} U^\dagger P_{\lambda_2} \otimes \sum_{h_1, h_2 \in \mathcal{M}} |h_1 + \mu_1\rangle\langle h_2 + \mu_2| \\
&= |\mathcal{M} + \mathcal{L}|^{-1} \sum_{\mu_1, \mu_2 \in \mathcal{L}} U P_{\mu_1} \rho P_{\mu_2} U^\dagger \otimes \sum_{h_1, h_2 \in \mathcal{M}} |h_1 + \mu_1\rangle\langle h_2 + \mu_2| \\
&= |\mathcal{M} + \mathcal{L}|^{-1} \sum_{\mu \in \mathcal{L}} U P_{\mu} \rho P_{\mu} U^\dagger \otimes \sum_{h \in \mathcal{M}} |h + \mu\rangle\langle h + \mu|,
\end{aligned}$$

where the last step uses the assumption of absence of coherence in  $\rho$ . The resulting reduced state is therefore

$$\text{Tr}_{\text{anc}} [\tilde{V}(\rho \otimes \eta) \tilde{V}^\dagger] = \sum_{\mu \in \mathcal{L}} \frac{|\mathcal{M}|}{|\mathcal{M} + \mathcal{L}|} U P_{\mu} \rho P_{\mu} U^\dagger = \frac{|\mathcal{M}|}{|\mathcal{M} + \mathcal{L}|} U \rho U^\dagger \approx_\delta \frac{|\mathcal{M}|}{|\mathcal{M} + \mathcal{L}|} \sigma \geq (1 - \delta) \sigma.$$

The claim now follows from the same estimate as in Case 1.  $\square$

We are now sufficiently equipped to approach the main result of this section. We write  $E(\rho) = \text{Tr}[H\rho]$  for the average energy of a state  $\rho$  on a system with Hamiltonian  $H$ .

**Theorem 6** (Asymptotic classification of states in thermodynamics). *For states  $\rho$  and  $\sigma$  on any quantum system of dimension  $d$  with given Hamiltonian  $H$ , the following are equivalent:*

- (a) *The states have equal entropy and average energy,  $S(\rho) = S(\sigma)$  and  $E(\rho) = E(\sigma)$ ,*
- (b) *There exists an ancilla system of size  $O(\sqrt{n \log n})$  whose Hamiltonian  $H_{\text{anc}}$  satisfies  $\|H_{\text{anc}}\| \leq O(n^{2/3})$  with state  $\eta$  as well as an energy-preserving unitary  $U$  such that*

$$\|\text{Tr}_{\text{anc}} [U(\rho^{\otimes n} \otimes \eta) U^\dagger] - \sigma^{\otimes n}\|_1 \xrightarrow{n \rightarrow \infty} 0. \tag{A10}$$

- (c) *There exists an ancilla system of size  $o(n)$  whose Hamiltonian  $H_{\text{anc}}$  satisfies  $\|H_{\text{anc}}\| \leq o(n)$  with states  $\eta$  and  $\nu$  as well as energy-preserving unitaries  $U$  and  $V$  such that*

$$\|\text{Tr}_{\text{anc}} [U(\rho^{\otimes n} \otimes \eta) U^\dagger - V(\sigma^{\otimes n} \otimes \nu) V^\dagger]\|_1 \xrightarrow{n \rightarrow \infty} 0. \tag{A11}$$

**Definition 7.** *When one (and hence all) of these conditions hold, we say that  $\rho$  is asymptotically equivalent to  $\sigma$ , and we write  $\rho \asymp \sigma$ .*

The bound on  $\|H_{\text{anc}}\|$  in condition (b) is not tight: our proof adapts straightforwardly if one replaces the exponent of  $2/3$  in by any other exponent strictly greater than  $1/2$ . We expect that the bound can be reduced even more, down to at least  $O(\sqrt{n \log n})$  as in Theorem 4, but proving this will probably require a more fine-grained arithmetical analysis of the energy levels.

Our interpretation of this result is essentially analogous to Theorem 4. The bound on  $\|H_{\text{anc}}\|$  is important in that without such a bound, we could transfer an arbitrary amount of energy to or from the ancilla while only modifying the system state marginally (embezzlement). Of course, none of this is specific to the observable under consideration being energy, and the theorem applies likewise to angular momentum or to any other observable. In fact, we expect the analogous theorem to hold for any finite number of commuting observables on the system that are required to be preserved by the unitaries, with very similar proof. The case of non-commuting observables may be more difficult.

*Proof.* From (c) to (a), equality of entropy follows from Theorem 4. Equality of energy follows from an estimate analogous to the estimate of entropy difference. With  $H^{(n)}$  being the  $n$ -qudit Hamiltonian and writing  $\varepsilon$  for the

left-hand side of (A11),

$$\begin{aligned}
|E(\rho) - E(\sigma)| &= \frac{1}{n} |E(\rho^{\otimes n}) - E(\sigma^{\otimes n})| \leq \frac{1}{n} |E(\rho^{\otimes n} \otimes \eta) - E(\rho^{\otimes n} \otimes \nu)| + 2 \frac{\|H_{\text{anc}}\|}{n} \\
&= \frac{1}{n} |E(U(\rho^{\otimes n} \otimes \eta)U^\dagger) - E(V(\rho^{\otimes n} \otimes \nu)V^\dagger)| + 2 \frac{\|H_{\text{anc}}\|}{n} \\
&\leq \frac{1}{n} |E(\text{Tr}_{\text{anc}}[U(\rho^{\otimes n} \otimes \eta)U^\dagger]) - E(\text{Tr}_{\text{anc}}[V(\sigma^{\otimes n} \otimes \nu)V^\dagger])| + 4 \frac{\|H_{\text{anc}}\|}{n} \\
&\leq \frac{1}{n} \varepsilon \|H^{(n)}\| + 4 \frac{\|H_{\text{anc}}\|}{n}
\end{aligned}$$

Since  $H^{(n)}$  is additive in  $n$ , we have  $\|H^{(n)}\| = n\|H\|$ , and the first term vanishes as  $\varepsilon \rightarrow 0$ . The second term vanishes as  $n \rightarrow \infty$  due to the assumption of sublinearity of  $\|H_{\text{anc}}\|$ . Note that the bound on  $H_{\text{anc}}$  now plays the role of the bound on entropy change due to the ancilla.

To see that (a) implies (b), we first apply Theorem 4. So for given  $\varepsilon > 0$ , we have  $n \in \mathbb{N}$  together with the other data such that

$$\text{Tr}_{\text{anc}}[U(\rho^{\otimes n} \otimes \eta)U^\dagger] \approx_\varepsilon \sigma^{\otimes n}. \quad (\text{A12})$$

We now need to find another unitary  $\tilde{U}$  that achieves something like (A12) while also being energy-preserving.

Let the spectral decomposition of the system's Hamiltonian be  $H = \sum_{i=1}^\ell E_i P_i$ , and let us assume that the Hamiltonian has been shifted such that  $E(\rho) = E(\sigma) = 0$  for simplicity. In order to impose strong energy typicality, let us consider the state  $\rho_{\text{typ}}$  obtained by restricting  $\rho^{\otimes n}$  such that a measurement of  $P_i^{(n)}$  will result in an outcome in the range  $n\text{Tr}[P_i \rho] \pm \sqrt{n \log n}$  with certainty. By taking  $n$  to be large enough, we can assume  $\rho^{\otimes n} \approx_\varepsilon \rho_{\text{typ}}$  by the central limit theorem. Let  $\mathcal{E}_\rho$  denote the set of energy levels of  $H^{(n)}$  on this typical subspace, and let us throw in their negatives and 0 for good measure,

$$\mathcal{L}_\rho := \mathcal{E}_\rho \cup (-\mathcal{E}_\rho) \cup \{0\}.$$

By construction, the set  $\mathcal{E}_\rho$  consists of all numbers of the form  $\sum_i c_i E_i$ , with integer coefficients  $c_i$  that satisfy  $|c_i - n\text{Tr}[P_i \rho]| \leq \sqrt{n \log n}$  for all  $i$ . Therefore, every number in  $\mathcal{L}_\rho$  is an integer linear combination of any nonzero fixed number in  $\mathcal{L}_\rho$  and the single-system energy levels  $E_i$ , using coefficients that are  $O(\sqrt{n \log n})$ . This implies that the  $k$ -fold Minkowski sum

$$k\mathcal{L}_\rho = \underbrace{\mathcal{L}_\rho + \dots + \mathcal{L}_\rho}_{k \text{ times}}$$

also contains only numbers given by some fixed number plus integer linear combinations of the energy levels  $E_i$  using coefficients of size  $O(k\sqrt{n \log n})$ . Therefore the cardinality  $|k\mathcal{L}_\rho|$  is at most polynomial,  $O(\text{poly}(nk))$ .

With  $\sigma_{\text{typ}}$  and  $\mathcal{L}_\sigma$  defined in the analogous manner and satisfying the analogous cardinality bound, let us put  $\mathcal{L} := \mathcal{L}_\rho \cup \mathcal{L}_\sigma$ , which then in particular contains all the energy levels that are typical for  $\rho$  or for  $\sigma$ . We have the bound

$$|k\mathcal{L}| = \left| \bigcup_{j=0}^k j\mathcal{L}_\rho + (k-j)\mathcal{L}_\sigma \right| \leq \sum_{j=0}^k |j\mathcal{L}_\rho| \cdot |(k-j)\mathcal{L}_\sigma| = O(\text{poly}(nk)),$$

so let us choose an exponent  $\gamma \in \mathbb{N}$  and a coefficient  $C > 0$  such that  $|k\mathcal{L}| \leq C(nk)^\gamma$  for all  $k$ ; the particular values are not important.

We now aim to apply Lemma 5 using  $\mathcal{M} := k\mathcal{L}$ . To determine a suitable value of  $k$ , we show that if  $n$  is sufficiently large, then there is  $k \leq n^{1/7}$  such that

$$|k\mathcal{L} + \mathcal{L}| \leq (1 + \varepsilon)|k\mathcal{L}|. \quad (\text{A13})$$

For if this was not the case, then we would have  $|(k+1)\mathcal{L}| > (1 + \varepsilon)|k\mathcal{L}|$ , which yields by induction on  $k$ ,

$$|k\mathcal{L}| \geq (1 + \varepsilon)^k |\mathcal{L}|.$$

For  $k = n^{1/7}$ , we would then be led to conclude

$$(1 + \varepsilon)^{n^{1/7}} |\mathcal{L}| \leq |n^{1/7} \mathcal{L}| \leq C(n^{8/7})^\gamma.$$

Since the left-hand side grows superpolynomially in  $n$  while the right-hand side grows only polynomially, this cannot be the case for all  $n$ . It follows that for suitably large  $n$ , there is  $k \leq n^{1/7}$  such that (A13) holds; let us fix such a  $k$ . We now equip the existing ancilla in (A12) with the trivial Hamiltonian  $H_{\text{anc}} := 0$ , so that also  $\rho_{\text{typ}} \otimes \eta$  is supported on the energy levels in  $\mathcal{L}$ . Because  $\text{Tr}_{\text{anc}}[U(\rho_{\text{typ}} \otimes \eta)U^\dagger]$  is  $3\varepsilon$ -close to  $\sigma_{\text{typ}}$ , which is also supported on the energy levels in  $\mathcal{L}$ , it follows that  $U(\rho_{\text{typ}} \otimes \eta)U^\dagger$  itself is already  $3\varepsilon$ -close to being supported on the energy levels in  $\mathcal{L}$ . Let us write  $\hat{\rho} := \rho^{\otimes n} \otimes \eta$  and  $\hat{\sigma}$  for the restriction of  $U(\rho_{\text{typ}} \otimes \eta)U^\dagger$  to the energy levels in  $\mathcal{L}$ , so that  $\hat{\sigma} \approx_{3\varepsilon} U\hat{\rho}U^\dagger$ . By taking  $\mathcal{M} := k\mathcal{L}$  in Lemma 5, we can therefore conclude the existence of an additional ancilla system  $\text{anc}'$  of size  $O(\log(|k\mathcal{L}|)) = O(\log n)$  with Hamiltonian bounded by  $4\|k\mathcal{L}\| = 4k\|\mathcal{L}\| \leq n^{1/7} \cdot O(\sqrt{n \log n}) < O(n^{2/3})$  as claimed, with an ancilla state  $\eta'$  and energy-preserving unitary  $\tilde{U}$  such that

$$\text{Tr}_{\text{anc}'}[\tilde{U}(\hat{\rho} \otimes \eta')\tilde{U}^\dagger] \approx_{12\varepsilon} \hat{\sigma}.$$

Putting all this together, we therefore have

$$\text{Tr}_{\text{anc}, \text{anc}'}[\tilde{U}(\rho^{\otimes n} \otimes \eta \otimes \eta')\tilde{U}^\dagger] = \text{Tr}_{\text{anc}, \text{anc}'}[\tilde{U}(\hat{\rho} \otimes \eta')\tilde{U}^\dagger] \approx_{12\varepsilon} \text{Tr}_{\text{anc}}[\hat{\sigma}] \approx_{3\varepsilon} \text{Tr}_{\text{anc}}[U\hat{\rho}U^\dagger] \approx_\varepsilon \sigma^{\otimes n},$$

resulting in a total trace distance difference between the left-hand side and the right-hand side of at most  $16\varepsilon$ .  $\square$

## Appendix B: Macroscopic thermodynamics as a resource theory

In the following, we use Theorem 6 in order to develop thermodynamics as a resource theory in the asymptotic limit, without assuming that any states come for free. This development is loosely based on the ideas of [33]. It is not yet to be understood as a definite treatment, and we will see that there are some loose ends which indicate how one might go about obtaining a definite treatment. We write  $Z_\beta = \text{Tr}[e^{-\beta H}]$  for the partition function.

The main results of this section are the following. We use the asymptotic equivalence (Theorem 6) to create a link between microscopic and macroscopic thermodynamics. In particular, we show how, given a system of identical and non-interacting particles, we can move from a description based on their quantum states to a description based uniquely on their energy and entropy. Then, we utilise our resource theory to analyse what state transformations can be achieved in the presence of a finite thermal reservoir and a battery, which leads us to our definition of work and heat. This analysis allows us to also investigate the efficiency of heat engines and refrigerators operating with finite-size reservoirs. Finally, we consider the situation in which the number of copies of a system can change, and we analyse the optimal rates of conversion between any two quantum states in our resource theory.

### 1. The energy-entropy diagram

Theorem 6 shows that it is only the energy and entropy of a state that determines its behaviour under many-copies transformations. Hence as far as the many-copies level is concerned, we can *identify* a state  $\rho$  with the pair of values  $(E(\rho), S(\rho)) \in \mathbb{R}^2$ . In order to understand thermodynamics as a resource theory asymptotically, we therefore need to ask: which pairs of numbers  $x = (x_E, x_S) \in \mathbb{R}^2$  do arise from a state in this manner? We call this set the *energy-entropy diagram*. The energy-entropy diagram depends on the system Hamiltonian  $H$ , and can be characterised as follows:

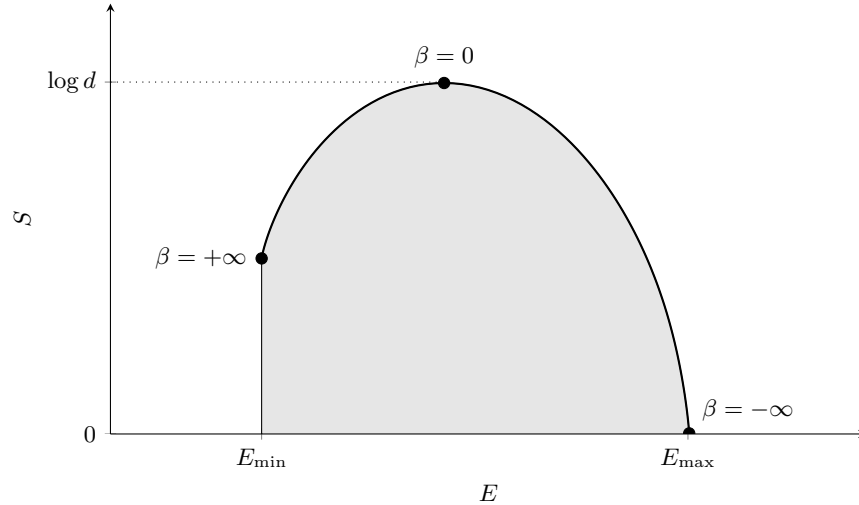


FIG. 2. Sketch of the energy-entropy diagram for a generic finite-dimensional quantum system. The energy-entropy diagram is the set of all points  $x = (x_E, x_S) \in \mathbb{R}^2$  which are achievable energy and entropy values in the sense that  $x_E = E(\rho)$  and  $x_S = S(\rho)$  for a suitable state  $\rho$ . The thick boundary curve is parametrised by the thermal states  $\tau_\beta = Z_\beta^{-1} e^{-\beta H}$ , starting with the ground state at  $\beta = +\infty$  at the lower left, passing through the maximally mixed (and maximal entropy) state at  $\beta = 0$ , and ending at maximal energy at parameter  $\beta = -\infty$ . The Hamiltonian used to generate this particular shape is  $H = |2\rangle\langle 2| + \sqrt{2}|3\rangle\langle 3|$  on  $\mathbb{C}^4$ , where the vertical drop at  $E_{\min}$  is due to a degenerate ground state. Compare e.g. [45, Fig. 1].

**Proposition 8.** *The values  $(E(\rho), S(\rho))$  form a convex subset of  $\mathbb{R}^2$  as in Figure 2, where the lower boundary is the line  $x_S = 0$  and the upper boundary is the curve  $\beta \mapsto (E(\tau_\beta), S(\tau_\beta))$  traced by the thermal states  $\tau_\beta = Z_\beta^{-1} e^{-\beta H}$  for  $\beta \in [-\infty, +\infty]$ .*

*Proof.* It is a standard fact that the states of maximal entropy for a given energy are precisely the thermal states. One way to see that this also holds for  $\beta < 0$  is by using the fact that it holds for  $\beta > 0$  and reversing the sign of the Hamiltonian.

It remains to show that also every smaller value of the entropy is achievable for a given energy. Clearly  $S = 0$  is achievable, namely by considering a pure state in a suitable superposition of energy levels which has the desired

expectation value of energy. Moreover, the set of all states of a given energy is a convex subset of all the density matrices, and in particular it is path-connected; since the map  $\rho \mapsto S(\rho)$  is continuous, it follows that also its image under  $S$  is path-connected, so that also all intermediate entropy values can be achieved for the given energy.

Convexity follows from the alternative characterisation in terms of linear inequalities that we will derive as Proposition 10.  $\square$

We use Cartesian coordinates  $x = (x_E, x_S)$  when speaking about a point in  $\mathbb{R}^2$  that may or may not belong to the energy-entropy diagram, and we also write  $x(\rho)$  when talking about the point  $(E(\rho), S(\rho))$  associated to a specific state  $\rho$ . Thus we have  $x(\rho)_E = E(\rho)$  and  $x(\rho)_S = S(\rho)$ , and the curve of thermal states is given by  $\beta \mapsto x(\tau_\beta)$ .

*Remark 9.* The curve of thermal states is parametrized by  $\beta \mapsto (E(\tau_\beta), S(\tau_\beta))$ , where

$$E(\tau_\beta) = \text{Tr} \left[ H Z_\beta^{-1} e^{-\beta H} \right] = -\frac{d \log Z_\beta}{d\beta}, \quad S(\tau_\beta) = -\text{Tr} \left[ Z_\beta^{-1} e^{-\beta H} \log(Z_\beta^{-1} e^{-\beta H}) \right] = \beta E(\tau_\beta) + \log Z_\beta.$$

Differentiating with respect to  $\beta$  and collecting terms results in the fundamental thermodynamic relation  $dS(\tau_\beta) = \beta dE(\tau_\beta)$ . For the energy-entropy diagram, this implies that the parameter  $\beta$  is precisely equal to the slope of the tangent at each point on the curve of thermal states.

By virtue of being convex and topologically closed, one can describe the energy-entropy diagram also in a dual way by writing down all the linear inequalities that bound it. These inequalities are most conveniently stated in terms of the quantities

$$A_\beta(x) := \beta x_E - x_S + \log Z_\beta, \tag{B1}$$

so that  $A_\beta(\tau_\beta) = 0$ . Note that  $A_\beta(x)$  is a linear function of  $x$ .

For a given value of  $\beta$ , we call  $A_\beta$  the  $\beta$ -athermality<sup>7</sup>, since it vanishes on the thermal state  $x(\tau_\beta)$ , and we think of  $A_\beta(x)$  as a measure of how far  $x$  is from being equal to  $x(\tau_\beta)$ . The  $\beta$ -athermality differs from the free energy  $x_E - \beta^{-1}x_S$  only by an additional factor of  $\beta$  and an additive constant. One of the reasons that we prefer using (B1) over the free energy is that on a state  $\rho$ , we can also neatly write it as the relative entropy distance to the thermal state,

$$A_\beta(x(\rho)) = D(\rho \| \tau_\beta), \tag{B2}$$

as one can see by writing out the definition of relative entropy and plugging in  $\tau_\beta = Z_\beta^{-1} e^{-\beta H}$ . This again justifies the term “ $\beta$ -athermality”. For  $\beta = 0$ , we obtain the negentropy  $A_0(x(\rho)) = \log d - S(\rho)$ .

We can now state the characterisation of the energy-entropy diagram by linear inequalities:

**Proposition 10.** *The energy-entropy diagram is the set of all points  $x \in \mathbb{R}^2$  such that  $x_S \geq 0$  and  $A_\beta(x) \geq 0$  for all  $\beta \in (-\infty, +\infty)$ .*

*Proof.* All the inequalities hold for an achievable point  $x = (E(\rho), S(\rho))$ , since both the entropy and the relative entropy (B2) are nonnegative.

In the other direction, we need to show that if  $x \in \mathbb{R}^2$  satisfies all the claimed inequalities, then it lies in the energy-entropy diagram. So by assumption, we have  $x_S \geq 0$  and

$$\beta x_E - x_S \geq \beta E(\tau_\beta) - S(\tau_\beta)$$

for all  $\beta \in \mathbb{R}$ . Taking  $\beta \rightarrow +\infty$  and  $\beta \rightarrow -\infty$  shows that we also must have  $E_{\min} \leq x_E \leq E_{\max}$ . Since there is a unique thermal state at every given energy in this range, there is a unique  $\beta$  such that  $E(\tau_\beta) = x_E$ . Using this  $\beta$ , we obtain from the previous inequality

$$x_S \leq S(\tau_\beta) + \beta(x_E - E(\tau_\beta)) = S(\tau_\beta),$$

so that  $x$  lies indeed below the curve traced by the thermal states in Figure 2.  $\square$

*Remark 11.* In Propositions 8 and 10, and in some of our upcoming results, we also consider negative temperatures, that is,  $\beta < 0$ . While thermal states at a negative temperature do not usually arise as a result of thermalisation, they still play an important roles in multiple physical effects (such as, for instance, in lasers, where coherent light amplification is obtained through population inversion) [45]. The main difference between thermal states at  $\beta > 0$  and  $\beta < 0$ , in our theory, is that the former are completely passive states from which we cannot extract energy by means of unitary operations, while the latter are active states, from which energy can be extracted.

<sup>7</sup> This terminology was suggested to us by Matteo Smerlak. Without the additive constant,  $A_\beta$  has also been called the “free entropy” in [36].



## 2. Thermodynamic variables and the convex cone of macrostates

In this section we introduce an additional macroscopic quantity to characterise the state of a thermodynamic system, referred to as *system size* or *amount of substance*. With this parameter we can fully characterise any thermodynamic transformation within our resource theory, since it allows for considering transformations in which the number of systems involved changes. For the purpose of our upcoming applications, let's consider what happens at the many-copies level.

**Proposition 12.** *For any  $n \in \mathbb{N}$ , the energy-entropy diagram of  $H^{(n)}$  equals the energy-entropy diagram of  $H$ , scaled up by a factor of  $n$ .*

*Proof.* Since  $E(\rho^{\otimes n}) = nE(\rho)$ , and similarly for  $S$ , it is clear that the energy-entropy diagram of  $H$ , when scaled by  $n$ , is contained in the energy-entropy diagram of  $H^{(n)}$ . The converse follows from Proposition 8, because any thermal state of  $H^{(n)}$  is an  $n$ -th tensor power of a thermal state of  $H$ .  $\square$

Together with Theorem 6, this also implies that for every  $n$ -system state  $\rho$  there is a single-system state  $\sigma$  such that  $\rho \preceq \sigma^{\otimes n}$  (that is,  $\rho$  is asymptotically equivalent to  $\sigma^{\otimes n}$ ), although  $\rho$  itself may be arbitrarily far from being a product state.

In order to keep track of  $n = n(\rho)$ , the number of copies of the system on which a state  $\rho$  lives, it is useful to consider the *triple* of numbers  $(E(\rho), S(\rho), n(\rho)) \in \mathbb{R}^3$ , for which we also write  $y(\rho)$ . Each component of this triple is an additive function of  $\rho$ , and therefore

$$y(\rho \otimes \sigma) = y(\rho) + y(\sigma). \quad (\text{B3})$$

By Theorem 6, the three components of  $y(\rho)$  provide a complete classification of single-system and multi-system states in thermodynamics—with given single-system Hamiltonian  $H$ —up to asymptotic equivalence.

Now we could consider the set of all points  $y = (y_E, y_S, y_n)$  that are of the form  $y = y(\rho)$  for some state  $\rho$ , and call it the *energy-entropy-size diagram* associated to the Hamiltonian  $H$ . But all of our results are only up to asymptotic equivalence, so that we effectively only consider states  $\rho$  with  $n(\rho) \gg 1$ . Equivalently, we can also work with small values of  $n$ , but then forget that  $n$  is required to be an integer by pretending that the system size can be an arbitrary nonnegative real number. We then still use the symbol “ $n$ ”, although it now plays the role of an “amount of substance”, just as in the ideal gas law  $pV = nRT$ . In principle, converting between number of microsystems and amount of substance involves rescaling by the Avogadro constant. This is indeed what we are doing here, except that we choose to measure the amount of substance with the unit in which the Avogadro constant is equal to 1. Based on this intuition, we thus define:

**Definition 13.** *The convex cone  $\text{Therm}(H)$  consists of all points  $y \in \mathbb{R}^3$  that are of the form  $y = n \cdot (x_E, x_S, 1)$  for some  $n \in \mathbb{R}_{\geq 0}$  and  $(x_E, x_S)$  in the energy-entropy diagram.*

In other words,  $\text{Therm}(H)$  is the convex cone that we obtain by taking the energy-entropy diagram in  $\mathbb{R}^2$  and applying the standard “homogenisation” trick for turning a convex set into a convex cone by adding an additional coordinate [46, p. 31]. We call a point  $y \in \text{Therm}(H)$  *normalised* if  $y_n = 1$ . Every nonzero  $y \in \text{Therm}(H)$  is a unique scalar multiple of a normalised point, so that for most purposes it is sufficient to consider normalised points only (see Section B 3).

*Remark 14.* If we slice  $\text{Therm}(H)$  at constant third coordinate  $n \in \mathbb{N}$  by considering all points of the form  $(x_E, x_S, n) \in \text{Therm}(H)$ , then this set is precisely the energy-entropy diagram of  $H^{(n)}$  thanks to Proposition 12.

*Remark 15.* Taking every (multi-system) state  $\rho$  to be represented by a point  $y(\rho) \in \text{Therm}(H)$  is a standard construction of thermodynamics: it corresponds to passing from the microstate to the macrostate. The thermodynamic variables of a macrostate are precisely<sup>8</sup> energy  $E$ , entropy  $S$ , and system size  $n$ , and the macrostate is specified completely by these three numbers. If one identifies the passage from microstate to macrostate with the information-theoretic many-copies limit, then our Theorem 6 offers a mathematically rigorous explanation for *why* the macroscopic variables are exactly these three and no others. There *are* many other extensive quantities that are invariant under energy-preserving unitaries—take the Rényi entropies or the variance of energy as examples. These quantities would indeed be relevant also macroscopically if we had required an *exact* conversion of  $\rho^{\otimes n}$  into  $\sigma^{\otimes n}$  for some  $n$ , possibly together with a sublinear ancilla. But our definition of many-copy equivalence allows for approximate conversions

---

<sup>8</sup> Of course this depends on which observables are considered to be conserved quantities. For us, as indicated by Theorem 6, energy is assumed to be the only observable that is conserved.

that get closer and closer to exact as  $n \rightarrow \infty$ . This is a more permissive notion of asymptotic equivalence, under which correspondingly fewer quantities are invariant, namely only the ones that are asymptotically continuous [34]. In the language of [27, 33], allowing such approximate conversions introduces an “epsilonfication”.

One may wonder how it is possible that the passage from microstate to macrostate within our idealised theory yields results that are so close to the standard one. For example, the class of allowed operations considered in our model is extremely wide, and moreover our results are valid in the many-copy limit. On the one hand, we are puzzled by the fact that we still recover the standard macroscopic description even though we are allowing for this large class of operations. On the other hand, instead, we consider the many-copy limit as a faithful enough description (at the macroscopic level) since the interactions between particles become small (they have an area scaling), compared to the extensive quantities (which have a volume scaling), as the number of particles grows to infinity. Moreover, results such as the von Neumann’s quantum ergodic theorem [47] help explain this phenomena.

Returning to technical developments, we extend the  $\beta$ -athermalities from  $\mathbb{R}^2$  to  $\mathbb{R}^3$  by setting

$$A_\beta(y) := \beta y_E - y_S + y_n \log Z_\beta. \quad (\text{B4})$$

On the energy-entropy diagram, which is embedded in  $\text{Therm}(H)$  as the set of all normalised points, this coincides with our previous definition of  $A_\beta(x)$ , and from there we extend linearly.

On an actual state  $\rho$ , we can again express the  $\beta$ -athermality as a relative entropy distance,

$$A_\beta(y(\rho)) = D(\rho \| \tau_\beta^{\otimes n(\rho)}),$$

where the  $n(\rho)$  appears because one needs to consider the thermal state on a suitable number of copies of the system.

The characterisation of the energy-entropy diagram by linear inequalities extends easily to  $\text{Therm}(H)$ :

**Proposition 16.** *The convex cone  $\text{Therm}(H)$  is the set of all  $y = (y_E, y_S, y_n) \in \mathbb{R}^3$  such that  $y_S \geq 0$  and  $A_\beta(y) \geq 0$  for all  $\beta \in (-\infty, +\infty)$ .*

*Proof.* Any point in  $\text{Therm}(H)$  satisfies these inequalities thanks to Proposition 10 together with the fact that  $A_\beta(\lambda y) = \lambda A_\beta(y)$  for all  $\lambda > 0$ , so that it is sufficient to consider normalised points  $y \in \text{Therm}(H)$  only. Conversely, suppose that  $y \in \mathbb{R}^3$  satisfies all these inequalities. Then from  $y_S \geq 0$  and  $A_0(y) = y_n \log d - y_S \geq 0$  we conclude  $y_n \geq 0$ . If it is the case that  $y_n = 0$ , then we conclude  $y_S = 0$ , and then also  $y_E = 0$  from considering  $A_\beta(y) \geq 0$  in the two limits  $\beta \rightarrow \pm\infty$ . Otherwise we have  $y_n > 0$ , and the point  $y_n^{-1}(y_E, y_S)$  satisfies all the inequalities necessary to lie in the energy-entropy diagram by Proposition 10, and therefore  $y \in \text{Therm}(H)$ .  $\square$

What this says is that there are two kinds of additive resource monotones that are relevant to thermodynamics:

- The entropy function  $\rho \mapsto S(\rho)$ ;
- The  $\beta$ -athermality functions  $\rho \mapsto A_\beta(\rho)$  indexed by  $\beta \in (-\infty, +\infty)$ .

In the terminology of [33, Section 7], these are *extremal* monotones. There are two more extremal monotones that one obtains by considering  $A_\beta$  as  $\beta \rightarrow \pm\infty$ , which results in the two functions

$$\rho \mapsto E(\rho) - n(\rho)E_{\min}, \quad \rho \mapsto n(\rho)E_{\max} - E(\rho).$$

It follows by [33, Corollary 7.9] that every other additive (and suitably continuous) monotone is a nonnegative linear combination or integral of these extremal ones.

### 3. Macroscopic thermodynamics as a general probabilistic theory

As we will illustrate in the upcoming subsections, pretty much any resource-theoretic question about macroscopic thermodynamics can be formulated and answered within the convex cone picture that we have developed. However, since the cone  $\text{Therm}(H) \subseteq \mathbb{R}^3$  may be a bit challenging to visualise, it helps the intuition to represent any macrostate  $y = (y_S, y_E, y_n) \in \text{Therm}(H)$  by the corresponding normalised macrostate  $x := y_n^{-1}(y_E, y_S)$  in the energy-entropy diagram, equipped with a weight of  $y_n$ . In this picture, combining systems as in (B3) corresponds to taking a convex combination of normalised macrostates, in the sense that

$$\frac{y(\rho \otimes \sigma)}{n(\rho \otimes \sigma)} = \frac{n(\rho)}{n(\rho \otimes \sigma)} \cdot \frac{y(\rho)}{n(\rho)} + \frac{n(\sigma)}{n(\rho \otimes \sigma)} \cdot \frac{y(\sigma)}{n(\sigma)}, \quad (\text{B5})$$

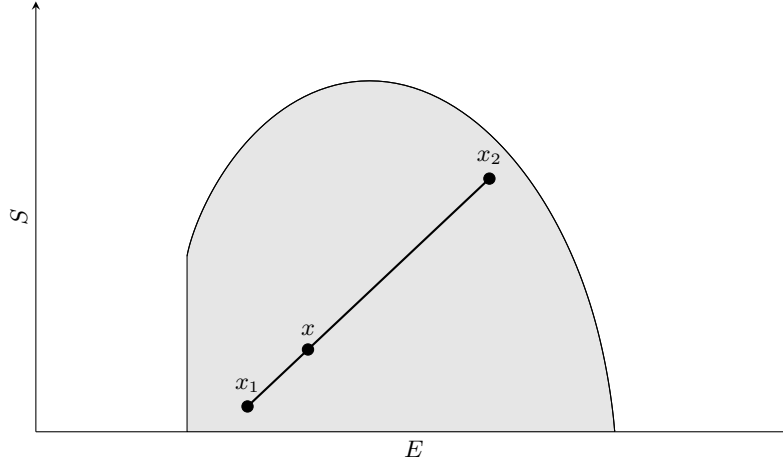


FIG. 3. Combining two systems in normalised macrostates  $x_1$  and  $x_2$  results in a total system in the normalised macrostate  $x$ , which is a convex combination of  $x_1$  and  $x_2$ , where the coefficient of  $x_1$ —proportional to the distance between  $x$  and  $x_1$ —is equal to the size of the first system relative to the total system, and similarly for  $x_2$ .

where  $\frac{y(\rho \otimes \sigma)}{n(\rho \otimes \sigma)}$ ,  $\frac{y(\rho)}{n(\rho)}$  and  $\frac{y(\sigma)}{n(\sigma)}$  are all normalised macrostates. Normalising by dividing by system size turns the energy and entropy coordinates, which are extensive quantities, into intensive quantities. While extensive quantities combine across subsystems additively, the associated intensive ones combine across subsystems via convex combinations with coefficients given by the relative subsystem sizes (Figure 3). This implies that everything that we do with the convex cone can alternatively be done directly in the energy-entropy diagram, by simply normalising the macrostates and keeping track of system size separately.

At the purely mathematical level, all of this is nicely analogous to the issue of normalisation of density matrices: it is usually more intuitive to assume the normalisation, and therefore one often normalises explicitly; but it is occasionally also advantageous to use unnormalised density matrices in order to keep track of the normalisation, which represents a “probability-to-occur”, analogous to our system size coordinate. Conversely, it is often useful to decompose a given normalised density matrix into a convex combination of other ones, such as pure states; many of the puzzling features of quantum theory can be attributed to the fact that such a decomposition is highly non-unique<sup>9</sup>. The same applies to thermodynamics: it may occasionally be useful to write a normalised macrostate  $x$  as a convex combination of other ones, or equivalently to decompose a given  $y \in \text{Therm}(H)$  into a sum  $y = y_1 + y_2$  for  $y_i \in \text{Therm}(H)$ . Of particular interest are decompositions into normalised macrostates that are extreme points of the energy-entropy diagram. Again such decompositions are highly non-unique, and this non-uniqueness is among the essential features of thermodynamics and underlies e.g. the possibility of constructing heat engines (Section B5). What this means is that macroscopic thermodynamics is, purely mathematically, an example of a *general probabilistic theory* [48–50]. The physical meaning, however, is very different from how one usually thinks of a general probabilistic theory such as quantum theory.

In more detail, Proposition 8 implies that the extreme points of the energy-entropy diagram are the following:

- The thermal macrostates  $x(\tau_\beta)$ , for  $\beta \in [-\infty, +\infty]$ , which are all different unless  $H = 0$ .
- The pure macrostate  $x(|E_{\min}\rangle\langle E_{\min}|)$ , which differs from the ground state  $x(\tau_\infty)$  only in the case of degeneracy, and the pure macrostate  $x(|E_{\max}\rangle\langle E_{\max}|)$ , which differs from the maximally excited state  $x(\tau_{-\infty})$  only in the case of degeneracy.

By first writing every normalised macrostate as a convex combination of a thermal state and a pure macrostate (Figure 4), and then decomposing the pure macrostate further into a combination of ground states and maximally excited states, we can represent every normalised macrostate as a convex combination of a suitable thermal state  $x(\tau_\beta)$  with  $x(|E_{\min}\rangle\langle E_{\min}|)$  and  $x(|E_{\max}\rangle\langle E_{\max}|)$ . For a given  $\beta$ , Figure 4 shows the region of normalised macrostates  $x$  that have a decomposition of this form. So we can write any  $y(\rho) \in \text{Therm}(H)$  as

$$\frac{y(\rho)}{n(\rho)} = c_\beta \cdot x(\tau_\beta) + c_{\min} \cdot x(|E_{\min}\rangle\langle E_{\min}|) + c_{\max} \cdot x(|E_{\max}\rangle\langle E_{\max}|),$$

<sup>9</sup> In the sense that two decomposition do in general not have a common refinement.

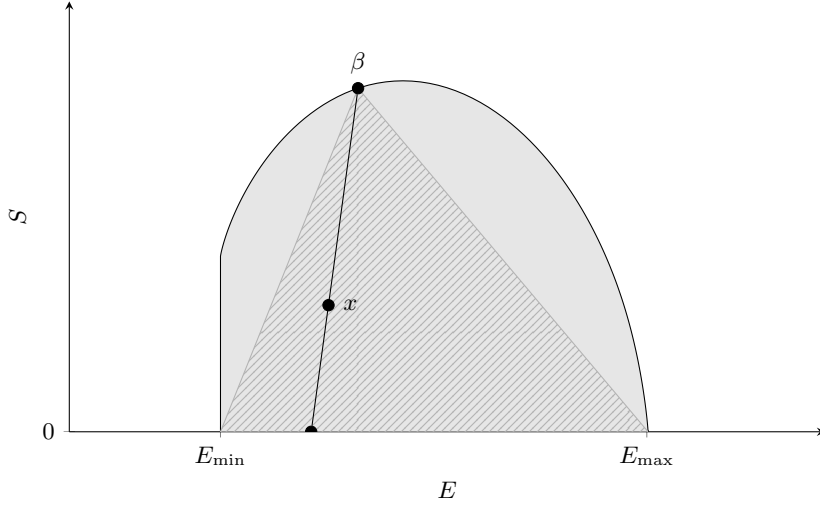


FIG. 4. Decomposing a normalised macrostate into a combination of the thermal macrostate at temperature  $\beta^{-1}$  and a pure macrostate, together with the set of all states that have such a decomposition at the given  $\beta$  (hatched).

for suitable weights  $c_\beta, c_{\min}, c_{\max} \in [0, 1]$ . If we choose rational approximations for these coefficients and suitably rescale the system size such that the product of each coefficient with  $n(\rho)$  is an integer, then we even obtain an asymptotic equivalence,

$$\rho \asymp \tau_\beta^{\otimes c_\beta n(\rho)} \otimes |E_{\min}\rangle\langle E_{\min}|^{\otimes c_{\min} n(\rho)} \otimes |E_{\max}\rangle\langle E_{\max}|^{\otimes c_{\max} n(\rho)}.$$

In this way, any state looks macroscopically like a combination of a number of thermal states (at one temperature), ground states, and maximally excited states. The non-uniqueness in this decomposition lies in the possibility of choosing the temperature  $\beta^{-1}$ ; the number of states of each kind in the decomposition will vary with that temperature. In practice, one can fix  $\beta$  first and then determine the coefficients by equating energy, entropy and system size of the two sides of the equation. If these coefficients turn out to be nonnegative, then one has found a feasible decomposition. This is an instance of decomposing a state in a general probabilistic theory into pure states.

In summary, at the mathematical level, macroscopic thermodynamics is a general probabilistic theory. Some of the essential features of thermodynamics are intimately related to the non-uniqueness of decompositions of states into extremal states—the same phenomenon that is behind many of the mysterious aspects of quantum theory. But although the mathematics is an instance of the formalism of general probabilistic theories, the physical meaning is very different from the standard interpretation of the latter [48].

#### 4. Work and heat

In this section we define and evaluate the amount of work and heat which is exchanged during an asymptotic state transformation in the presence of a finite thermal reservoir and a battery. The results we obtain, Eqs. (B9) and (B10), are analogous to the standard ones, but depend on an effective temperature which does not have to be equal to the temperature of the reservoir. But when the size of the reservoir tends to infinity, then the amount of work and heat exchanged coincides with the standard one.

In Theorem 6, we have seen that states with the same average energy and entropy can be asymptotically converted into one another, without any exchange of energy. We now consider the case in which we are given a state  $\rho$  and a state  $\sigma$  with possibly different entropy and average energy; for simplicity, we consider the case  $n(\rho) = n(\sigma) = 1$  only. By Theorem 6, we cannot in general asymptotically convert  $\rho$  into  $\sigma$  as states of a closed system, but what if we allow the system to interact with its environment? More precisely, we consider this environment to consist of two subsystems that we call “thermal reservoir” and “battery”, due to the roles that they play in our considerations. As before, each subsystem consists of any number of microsystems with Hamiltonian  $H$ . Assuming an environment to consist of a reservoir plus battery is motivated also by the decomposition of any macrostate into a thermal and a pure part as in the previous subsection.

We assume that the thermal reservoir consists initially of  $m$  copies of the thermal state at some temperature  $\beta_1^{-1}$ ,

and the battery of  $\ell$  copies of a pure ground state. The initial state of the total system is therefore given by

$$\omega_{\text{in}} = \rho^{\otimes n} \otimes \tau_{\beta_1}^{\otimes m} \otimes |E_{\text{min}}\rangle\langle E_{\text{min}}|^{\otimes \ell}. \quad (\text{B6})$$

Since  $\rho$  and  $\sigma$  may have different entropy and average energy, turning the former into the latter means that we also have to modify the reservoir and battery states. In fact, in order to convert  $\rho$  into  $\sigma$ , we apply Theorem 6 to the final state of all three subsystems, which we assume to be close to

$$\omega_{\text{fin}} = \sigma^{\otimes n} \otimes \tau_{\beta_2}^{\otimes m} \otimes |E_{\text{max}}\rangle\langle E_{\text{max}}|^{\otimes \ell}, \quad (\text{B7})$$

where now the reservoir is at a possibly different temperature  $\beta_2^{-1}$  and the battery is in the maximally excited state. We choose the final state to have this form with the reservoir in a thermal state, because otherwise additional work could be extracted from it (at least in the limit  $m \gg 1$ , which is what we assume). Thus, assuming the final state of the reservoir to be thermal allows us to study the ultimate bounds for the work exchanged during a state transformation in the presence of a finite size reservoir (finite in a sense that will be clear later in the section). If our results were not in the asymptotic limit, then we could have replaced the thermal state with a passive state. Although this kind of analysis falls outside the goals of this paper, we nevertheless think that it should be explored in subsequent works on this topic.

So overall, we consider  $\rho$  and  $\sigma$  as given, as well as the inverse temperatures  $\beta_1$  and  $\beta_2$ , while  $m$  and  $\ell$  need to be determined such that the transformation is possible. It may help to visualise how the macrostates associated to Eqs. (B6) and (B7) arise as convex combinations in the energy-entropy diagram.

Now in order for Theorem 6 to apply, we need to consider the asymptotic limit, that is, when  $n$ ,  $m$ , and  $\ell \gg 1$ . In this case, we can convert  $\omega_{\text{in}}$  into  $\omega_{\text{fin}}$  using the set of allowed operations if and only if they have the same average energy and entropy; conservation of system size is already guaranteed to hold. This results in two equations that we can solve for  $m$  and  $\ell$ , resulting in

$$\frac{m}{n} = \frac{S(\sigma) - S(\rho)}{S(\tau_{\beta_1}) - S(\tau_{\beta_2})}, \quad (\text{B8})$$

and a somewhat more complicated expression for  $\frac{\ell}{n}$ . So in order for  $m$  to be nonnegative, we should have  $\beta_1 < \beta_2$  if  $S(\rho) > S(\sigma)$  and vice versa (assuming that  $\beta_1, \beta_2 > 0$ ). Physically, this implies that when we dump entropy from the system into the thermal reservoir, we increase its temperature, and vice versa, as we would expect in the case of a finite size thermal reservoir. We refer to our thermal reservoir as being of finite size because, even if it is composed of  $m \rightarrow \infty$  copies, the reservoir size is finite *relative to* the system size  $n$ , in contrast to the case analysed in [5]. Similarly, a positive value  $\ell > 0$  means that we achieve an extraction of work from the system; while if  $\ell$  comes out negative, then we can make it positive by taking the initial state of the battery to be  $|E_{\text{max}}\rangle^{\otimes \ell}$ , and the final one  $|E_{\text{min}}\rangle^{\otimes \ell}$ , which corresponds to an injection of work into the system. For simplicity, we focus on the case that  $m, \ell > 0$  with  $\omega_{\text{in}}$  and  $\omega_{\text{fin}}$  as above, while the other cases are analogous.

We can now evaluate the work extracted and heat provided during the state transformation. We identify these two quantities with, respectively, the energy difference between the final and initial  $\ell$  copies of pure states, and with the energy difference between the initial and final  $m$  copies of thermal states. Thus, work is the energy stored inside the pure states, and heat is the energy exchanged with the thermal states. Using the result of Eq. (B8), we obtain the following expressions for the work extracted and the heat provided per copy of  $\rho$  and  $\sigma$ ,

$$W_{\beta_1, \beta_2}(\rho \rightarrow \sigma) = \frac{\ell}{n} (E_{\text{max}} - E_{\text{min}}) = (E(\rho) - E(\sigma)) - \frac{E(\tau_{\beta_1}) - E(\tau_{\beta_2})}{S(\tau_{\beta_1}) - S(\tau_{\beta_2})} (S(\rho) - S(\sigma)), \quad (\text{B9})$$

$$Q_{\beta_1, \beta_2}(\rho \rightarrow \sigma) = \frac{m}{n} (E(\tau_{\beta_1}) - E(\tau_{\beta_2})) = \frac{E(\tau_{\beta_1}) - E(\tau_{\beta_2})}{S(\tau_{\beta_1}) - S(\tau_{\beta_2})} (S(\sigma) - S(\rho)). \quad (\text{B10})$$

These quantities depend on the initial and final system state, but also on the initial and final temperature of the reservoir. The definition we use for work and heat is consistent with the first law of thermodynamics, since we have  $\Delta E(\rho \rightarrow \sigma) = Q_{\beta_1, \beta_2}(\rho \rightarrow \sigma) - W_{\beta_1, \beta_2}(\rho \rightarrow \sigma)$ , where  $\Delta E = E(\rho) - E(\sigma)$  is the average energy difference between the final and initial state of the system, independently of  $\beta_1$  and  $\beta_2$ .

These equations for work and heat are similar to the standard ones. In fact, work is given by the free energy difference between  $\rho$  and  $\sigma$ , for an external effective temperature  $\beta_{\text{eff}}^{-1}$  depending on the initial and final temperatures of the thermal reservoir,

$$\beta_{\text{eff}}(\beta_1, \beta_2) = \frac{S(\tau_{\beta_1}) - S(\tau_{\beta_2})}{E(\tau_{\beta_1}) - E(\tau_{\beta_2})}, \quad (\text{B11})$$

so that

$$W_{\beta_1, \beta_2}(\rho \rightarrow \sigma) = \beta_{\text{eff}}^{-1}(A_{\beta_{\text{eff}}}(\rho) - A_{\beta_{\text{eff}}}(\sigma)).$$

In the same way, the equation for heat is equal to the standard one, for the same effective temperature  $\beta_{\text{eff}}^{-1}$ ,

$$Q_{\beta_1, \beta_2}(\rho \rightarrow \sigma) = \beta_{\text{eff}}^{-1}(S(\sigma) - S(\rho)).$$

This equation can also be seen as a non-infinitesimal generalisation of the fundamental thermodynamic relation  $dQ = \beta^{-1}dS$ . Also, by the defining Eq. (B11), the effective temperature  $\beta_{\text{eff}}^{-1}$  can be visualised as a slope in the energy-entropy diagram, as in Figure 5.

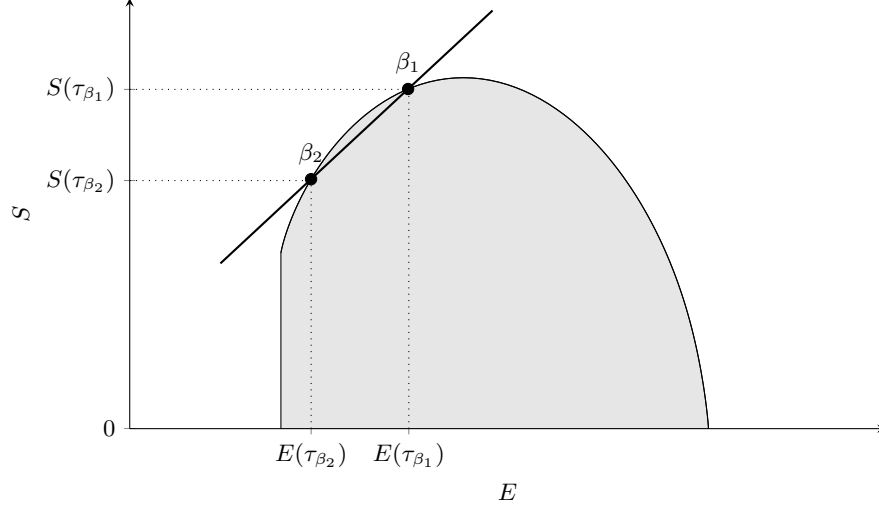


FIG. 5. The visualisation of the effective inverse temperature of the reservoir,  $\beta_{\text{eff}}$ . The thermal reservoir initially consists of  $m$  copies of  $\tau_{\beta_1}$ , which are turned into  $\tau_{\beta_2}$  by the state transformation. The two macrostates are highlighted on the border of the energy-entropy diagram. The value of  $\beta_{\text{eff}}$  is given by the slope of the line connecting these two points. When  $\beta_2 = \beta_1 + \varepsilon$ , for  $|\varepsilon| \rightarrow 0$ , the two points get closer and closer, and the line approaches the tangent to the curve of thermal states. In this case,  $\beta_{\text{eff}} = \beta_1 + O(\varepsilon)$ , by Remark 9.

Let us now consider the limiting case of an infinite reservoir, so that the reservoir temperature changes only infinitesimally. In this case, we have  $\beta_2 = \beta_1 + \varepsilon$ , where  $|\varepsilon| \ll 1$ . Then, it is straightforward to show that  $\beta_{\text{eff}} = \beta_1 + O(\varepsilon)$ , and the work and heat we obtain are equal to the standard ones (up to first order in  $\varepsilon$ ), that is,

$$W_{\text{standard}}(\rho \rightarrow \sigma) = \beta_1^{-1}(A_{\beta_1}(\rho) - A_{\beta_1}(\sigma)) + O(\varepsilon),$$

$$Q_{\text{standard}}(\rho \rightarrow \sigma) = \beta_1^{-1}(S(\sigma) - S(\rho)) + O(\varepsilon).$$

Moreover, we find from Eq. (B8) that, when we *want* the temperature change to be only  $\varepsilon \ll 1$ , then the required size of the thermal reservoir per copy of the system  $S$  tends to infinity, according to

$$\frac{m}{n} = \frac{S(\sigma) - S(\rho)}{\beta_1 \langle \Delta^2 H \rangle_{\tau_{\beta_1}}} \frac{1}{\varepsilon} + O(1), \quad (\text{B12})$$

where the expectation value in the denominator is the variance of energy in the state  $\tau_{\beta_1}$ , or equivalently  $\beta_1^{-2}$  times the heat capacity (at  $\beta_1$ ) of a single system.

One might be also interested in the maximum work that can be extracted from a quantum state when the thermal reservoir is absent [51]. In this case, we can set  $m = 0$  in Eqs. (B6) and (B7), so that the overall system is composed by the system of interest and the battery. From Eq. (B8) we obtain that the final state  $\sigma$  has to have the same entropy of the initial one, that is,  $S(\rho) = S(\sigma)$ . If we want to extract the maximum amount of work, the final state of the system has to be thermal [52]. Thus, we obtain  $\sigma = \tau_{\tilde{\beta}}$ , where the temperature  $\tilde{\beta}^{-1} > 0$  is such that  $S(\tau_{\tilde{\beta}}) = S(\rho)$ . Then, from Eq. (B9) we find the amount of work that we can asymptotically extract from  $\rho$ , per single copy of the state,

$$W_{\text{max}}(\rho) = E(\rho) - E(\tau_{\tilde{\beta}}), \quad (\text{B13})$$

in agreement with previous results [53]. Also in this case, it is simple to read off the result we obtain from the energy-entropy diagram. In fact, the maximal amount of pure energy that can be extracted,  $\ell(E_{\max} - E_{\min})$ , is given by the horizontal distance between the macrostate  $x(\rho)$  and the curve of thermal states, multiplied by the system size  $n$ .

## 5. Heat Engines

We now show how the results of the previous section can be used, together with Theorem 6, in order to analyse the efficiency of heat engines (and refrigerators) utilising finite size reservoirs. We do not assume any specific kind of engine consisting of a particular device or using particular mechanisms; instead, we utilise our formalism in order to derive the maximal efficiency of *any* protocol operating on two finite size reservoirs. As before, our analysis is valid in the limit of many copies and in the case where all systems consist of (approximately) non-interacting microsystems with common Hamiltonian  $H$ . We find that, when the reservoirs utilised by heat engines and refrigerators have a finite size, the efficiency of these machines depends on two effective temperatures (describing the hot and cold reservoirs, respectively). In particular, as we can observe in Eqs. (B16) and (B17), the optimal efficiency of heat engines and refrigerators interacting with finite-size reservoirs is always lower than the Carnot efficiency.

Our model consists of the same tripartite system as in the previous section, but further specialised to the case where both the initial state  $\rho$  and the final state  $\sigma$  are themselves thermal. Hence the initial state is given by

$$\omega_{\text{in}}^{\text{engine}} = \tau_{\beta_{\text{cold}}}^{\otimes n} \otimes \tau_{\beta_{\text{hot}}}^{\otimes m} \otimes |E_{\min}\rangle\langle E_{\min}|^{\otimes \ell}, \quad (\text{B14})$$

where  $\beta_{\text{cold}} > \beta_{\text{hot}}$ . The final state, instead, is

$$\omega_{\text{fin}}^{\text{engine}} = \tau_{\beta_{\text{less-cold}}}^{\otimes n} \otimes \tau_{\beta_{\text{less-hot}}}^{\otimes m} \otimes |E_{\max}\rangle\langle E_{\max}|^{\otimes \ell}, \quad (\text{B15})$$

where  $\beta_{\text{cold}} > \beta_{\text{less-cold}} > \beta_{\text{less-hot}} > \beta_{\text{hot}}$ . The engine uses the hot and cold reservoirs to extract work, but in the meanwhile it degrades these reservoirs, assimilating their temperatures (because these are of finite size).

Since everything that we do is reversible, one can consider both the transformation  $\omega_{\text{in}}^{\text{engine}} \rightarrow \omega_{\text{fin}}^{\text{engine}}$  (heat engine) as well as the reverse  $\omega_{\text{fin}}^{\text{engine}} \rightarrow \omega_{\text{in}}^{\text{engine}}$  (refrigerator). We are not concerned with the question of how to realise these transformations; Theorem 6 gives us necessary and sufficient conditions for when they are realisable, but does not make any statement about how to implement them, using a “working body” or otherwise. We only know that there exists some unitary acting on the global system together with a small number of ancilla systems which realises these devices to any desired degree of accuracy as  $m, n, \ell \rightarrow \infty$ .

In order to evaluate the efficiency of these two devices, we need to evaluate the heat exchanged with the hot reservoir, the work produced or utilised, and the heat exchanged with the cold reservoir. Due to reversibility, these quantities are the same for both devices (at least in absolute value). Using Eqs. (B9) and (B10), we find the heat exchanged with the hot reservoir  $Q_{\text{hot}}$ , and the work exchanged  $W$ ,

$$Q_{\text{hot}} = \frac{E(\tau_{\beta_{\text{hot}}}) - E(\tau_{\beta_{\text{less-hot}}})}{S(\tau_{\beta_{\text{hot}}}) - S(\tau_{\beta_{\text{less-hot}}})} (S(\tau_{\beta_{\text{less-cold}}}) - S(\tau_{\beta_{\text{cold}}})),$$

$$W = (E(\tau_{\beta_{\text{cold}}}) - E(\tau_{\beta_{\text{less-cold}}})) - \frac{E(\tau_{\beta_{\text{hot}}}) - E(\tau_{\beta_{\text{less-hot}}})}{S(\tau_{\beta_{\text{hot}}}) - S(\tau_{\beta_{\text{less-hot}}})} (S(\tau_{\beta_{\text{cold}}}) - S(\tau_{\beta_{\text{less-cold}}})),$$

both per copy of the first reservoir system. On the other hand, since the system  $S$  is now the cold reservoir, the heat  $Q_{\text{cold}}$  exchanged with it per copy is equal to

$$Q_{\text{cold}} = E(\tau_{\beta_{\text{less-cold}}}) - E(\tau_{\beta_{\text{cold}}}).$$

We can now evaluate the efficiency of the heat engine, defined as  $\eta_{\text{engine}} = \frac{W}{Q_{\text{hot}}}$ , and the efficiency of the refrigerator,  $\eta_{\text{refrigerator}} = \frac{Q_{\text{cold}}}{W}$ . We find that the efficiencies are equal to

$$\eta_{\text{engine}} = 1 - \frac{\beta_{\text{eff}}(\beta_{\text{hot}}, \beta_{\text{less-hot}})}{\beta_{\text{eff}}(\beta_{\text{cold}}, \beta_{\text{less-cold}})}, \quad (\text{B16})$$

$$\eta_{\text{refrigerator}} = \left( \frac{\beta_{\text{eff}}(\beta_{\text{cold}}, \beta_{\text{less-cold}})}{\beta_{\text{eff}}(\beta_{\text{hot}}, \beta_{\text{less-hot}})} - 1 \right)^{-1}, \quad (\text{B17})$$

where  $\beta_{\text{eff}}$  was defined in Eq. (B11). In terms of the interpretation of effective inverse temperatures as slopes in the

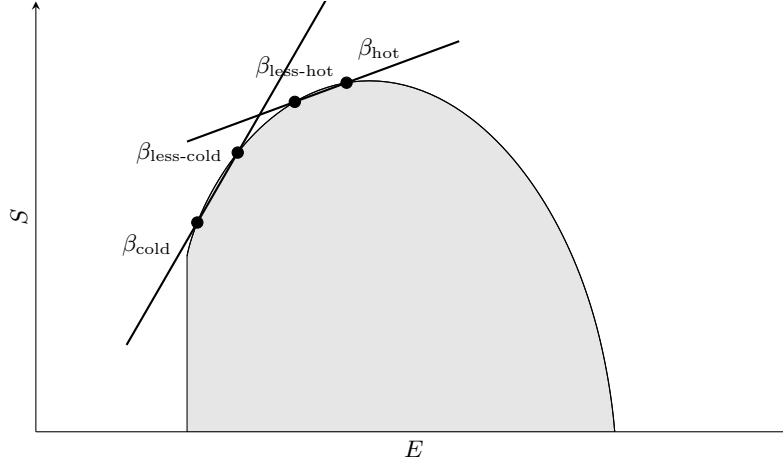


FIG. 6. The two effective temperatures that determine engine efficiency interpreted as slopes in the energy-entropy diagram. For  $\beta_{\text{ess-cold}}$  very close to  $\beta_{\text{cold}}$  and  $\beta_{\text{ess-hot}}$  very close to  $\beta_{\text{hot}}$ , i.e. when the reservoirs are very large compared to the battery size, then the lines approximate tangents and the resulting efficiency approaches the Carnot efficiency.

energy-entropy diagram, we can understand these efficiencies as in Figure 6: for example for the heat engine, the quotient of the slopes is always less than the quotient of the two tangent slopes at  $\beta_{\text{hot}}$  and  $\beta_{\text{cold}}$ , respectively. This implies that  $\eta_{\text{engine}} < 1 - \frac{\beta_{\text{hot}}}{\beta_{\text{cold}}}$ , and similarly  $\eta_{\text{refrigerator}} < \left( \frac{\beta_{\text{ess-cold}}}{\beta_{\text{ess-hot}}} - 1 \right)^{-1}$ , so that both efficiencies are strictly lower than the Carnot efficiencies. This is due to the fact that the temperature of the two finite size reservoirs changes during the process. In the limit where the temperature of the two reservoirs changes only by an infinitesimal amount, both efficiencies approach Carnot's values.

## 6. Optimal rates of conversion and how to compute them

So far, we have only considered asymptotic equivalence of state, since only energy-preserving unitaries have been allowed. What do we get if we allow in addition that subsystems can be discarded? Building on our previous results, we will now give one possible answer to this question. In all cases, we assume that a state  $\rho$  lives on a certain number  $n(\rho)$  of microsystems as before, and when we are dealing with two (or more) states  $\rho$  and  $\sigma$ , we do not assume  $n(\rho) = n(\sigma)$ .

**Lemma 17** (The asymptotic ordering  $\succeq$ ). *For given states  $\rho$  and  $\sigma$ , the following are equivalent:*

- (a) *There is a state  $\phi$  such that  $\rho \asymp \sigma \otimes \phi$  in the sense of Theorem 6.*
- (b) *There is a state  $\sigma' \asymp \rho$  such that  $\text{Tr}_{\text{sub}}[\sigma'] = \sigma$  for some subsystem that is not entangled with the rest.*
- (c)  *$S(\rho) \geq S(\sigma)$  and  $A_\beta(\rho) \geq A_\beta(\sigma)$  for all  $\beta \in (-\infty, +\infty)$ .*
- (d) *We have  $y(\rho) - y(\sigma) \in \text{Therm}(H)$ .*

Let us write  $\rho \succeq \sigma$  for the ordering relation on states corresponding to these equivalent conditions. In the following, we will investigate this ordering relation a bit further.

*Proof.* The implication from (a) to (b) is simply by taking  $\sigma' := \sigma \otimes \phi$ .

Next, we show that (b) implies (c); this follows from the fact that the additive monotones  $S$  and  $A_\beta$  respect asymptotic equivalence  $\asymp$ , and are nonincreasing under tracing out such subsystems. The former is a consequence of Theorem 6, while the latter is a consequence of the no-entanglement assumption in the case of  $S$  (the conditional entropy is nonnegative) and of the data processing inequality in the case of  $A_\beta$ ,

$$A_\beta(\rho) = D(\rho \| \tau_\beta^{\otimes n(\rho)}) \geq D\left(\text{Tr}_{\text{sub}}[\rho] \middle\| \text{Tr}_{\text{sub}}\left[\tau_\beta^{\otimes n(\rho)}\right]\right) = A_\beta(\text{Tr}_{\text{sub}}[\rho]),$$

where the last equation holds because  $\text{Tr}_{\text{sub}}[\tau_\beta]$  is the thermal state on the subsystem.



From (c) to (d), the point  $y(\rho) - y(\sigma)$  satisfies all the inequalities of Proposition 16 by assumption, and therefore lies in  $\text{Therm}(H)$ .

From (d) to (a), the assumption together with Remark 14 guarantees the existence of a state  $\phi$  with  $y(\phi) = y(\rho) - y(\sigma)$ . Therefore  $y(\rho) = y(\sigma \otimes \phi)$ , and then  $\rho \succeq \sigma \otimes \phi$  is a consequence of Theorem 6.  $\square$

The “no entanglement” requirement in condition (b) seems a bit artificial, and it would be interesting to obtain results analogous to the upcoming ones for the ordering relation defined in the analogous way, but where one would be allowed to trace out an *arbitrary* subsystem. We suspect that such a development would require generalisations of Theorems 4 and 6, where instead of characterising the asymptotic equivalence of states relative to energy-preserving unitaries, one would instead classify the asymptotic *ordering* of states relative to energy-preserving unitaries and discarding subsystems. We currently do not have such a result and thus use the  $\succeq$  relation from Lemma 17.

**Definition 18** ([33, Eq. (8.3)]). *The maximal rate of converting a state  $\rho$  into a state  $\sigma$  is given by*

$$R_{\max}(\rho \rightarrow \sigma) := \sup \left\{ \frac{m}{n} \mid \rho^{\otimes n} \succeq \sigma^{\otimes m} \right\} \quad (\text{B18})$$

So roughly speaking, we now ask: if we try to convert many copies of  $\rho$  into many copies of  $\sigma$ , then how many copies of  $\rho$  do we need per copy of  $\sigma$ , where we may discard some additional “junk” states in the process?

Since we already have allowed for sublinear ancillas in the definition of asymptotic equivalence, this notion of maximal rate actually corresponds to the notion of *regularised* maximal rate of [33, Section 8]. Building on the methods that we have developed so far, it is not hard to write down a concrete formula for computing maximal rates:

**Theorem 19.** *The maximal rate from  $\rho$  to  $\sigma$  can be computed in two ways:*

- (a)  $R_{\max}(\rho \rightarrow \sigma)$  is equal to the value of  $r$  at which the line in  $\mathbb{R}^3$  defined by  $r \mapsto y(\rho) - ry(\sigma)$  pinches the boundary of the cone  $\text{Therm}(H)$ , so that

$$R_{\max}(\rho \rightarrow \sigma) = \max \{ r \in \mathbb{R}_{\geq 0} \mid y(\rho) - ry(\sigma) \in \text{Therm}(H) \}. \quad (\text{B19})$$

- (b)  $R_{\max}(\rho \rightarrow \sigma)$  is also equal to the minimal ratio of the value of an additive monotone on  $\rho$  versus its value on  $\sigma$ ,

$$R_{\max}(\rho \rightarrow \sigma) = \min \left\{ \frac{S(\rho)}{S(\sigma)}, \inf_{\beta \in (-\infty, +\infty)} \frac{A_\beta(\rho)}{A_\beta(\sigma)} \right\}, \quad (\text{B20})$$

where the minimization is only over those fractions for which the denominator is nonzero.

*Proof.* By additivity of  $y$ , a rational number  $r = \frac{p}{q} \in \mathbb{Q}_{\geq 0}$  is an achievable rate if and only if  $qy(\rho) - py(\sigma) \in \text{Therm}(H)$ , or equivalently  $y(\rho) - ry(\sigma) \in \text{Therm}(H)$ . This implies (B19).

One gets (B20) from (B19) via Proposition 16, since  $y(\rho) - ry(\sigma) \in \text{Therm}(H)$  is equivalent to  $S(\rho) \geq rS(\sigma)$  together with  $A_\beta(\rho) \geq rA_\beta(\sigma)$  for all  $\beta \in (-\infty, +\infty)$ . Hence the condition on  $r$  is that it must be less than or equal to  $\frac{S(\rho)}{S(\sigma)}$ , and also less than or equal to  $\frac{A_\beta(\rho)}{A_\beta(\sigma)}$  for every  $\beta$ , for those fractions for which the denominator is nonzero. The largest  $r$  that satisfies this is precisely (B20).  $\square$

To understand Eq. (B19) intuitively, it may help to normalise the macrostates and phrase the condition in terms of convex combinations in the energy-entropy diagram instead, as per Section B 3.

What makes the infimum over  $\beta$  in Eq. (B20) nontrivial to evaluate is the presence of the partition function term  $\log Z_\beta$  in both the numerator and the denominator, due to Eq. (B4). Nevertheless, this is a very explicit formula with which one should be able to compute rates in practice. It is an instance of [33, Theorem 8.24], and the proof is correspondingly similar.